# Chapter - 2

# Experimental Method

## 2.1. Introduction

In this chapter, the basic information of combustion synthesis method is explained with its principle, useful parameters, theoretical background and recent scope of the synthesis method in material science and technology. The detailed procedure to prepare phosphors required, materials, sample preparation has been explained in this chapter.

## 2.2. Combustion Synthesis Method

### 2.2.1. Overview

Combustion synthesis method generally called as self-propagating high-temperature synthesis, was discovered in the 1980s. It is mainly a wet-chemical processing method. It does not require additional calcination of the material and repetitive heating treatment. Combustion synthesis method was accidentally discovered by Prof. Patil in his laboratory in India in 1988 [1]. Combustion synthesis method is an efficient and inexpensive method for the production of highly crystalline materials like inorganic-ceramic phosphor, magnetic materials, etc [2, 3]. The crystalline materials can be prepared with controlled particle size specifically of the order of micrometer to nanometre, and having a composition to assemble them together into large frame of structures with extraordinary properties and different functions [4, 5]. It is an extensively useful method to develop materials in all section for commercial and industrial applications. It is one of the most popular method that draw attention from the scientists and material technologists of various disciplines since last three decades. The physical properties like structure having crystalline or amorphous, purity of material, surface area, particle size, porosity and agglomeration of the synthesized powders which highly depends on the parameters adopted for the process [3, 6].

There are several methods such as solution synthesis method, solid-solid reaction method and combustion method to develop various materials having large area of applications in day to day life. The aim of all these synthesis processes is mainly to manufacture high purity materials having fine particle shape and size with a low agglomeration as well as low production costs [7-9]. The selection of synthesis process to develop of materials may depend on the application of the material, and also the reagents that are used for doping purpose. Combustion method is widely preferred for the preparation of phosphors having pure crystalline phase and homogeneous crystalline powders of inorganic metal oxides, pyrophosphates, borates, and vanadate, etc. Combustion synthesis method can make use of the salts of the metallic reagents such as phosphate, nitrate, metal vanadate, sulphate, tungstate, and carbonate, as oxidant. Glycine, citric acid, sucrose, boric acid, urea, and other water-soluble carbohydrates are used as reducing reagents which can act as fuels in the combustion process [10]. The reagent salts will act as an oxidizer in the combustion reaction for the fuel, as a result, the obtained powder can pyrolysed in product of a pure single phase. In some cases of combustion reaction, it needs consequent heating treatment to get single-phase [11, 12]. The combustion synthesis can take place as either in the volume or from of layer to layer transmission of combustion modes depending upon the type of reagents taken in the process, as well as the thermal treatment used for the combustion process [13]. This treatment not only intensifies the crystallinity of the materials but also allows homogeneity of the rare-earth impurity ions inside the host material in a single step [14]. Recently the rare earth doped phosphors based on semiconducting materials is new area of research using high-temperature combustion synthesis method. Currently, wide range of phosphors based on inorganic materials were prepared by combustion synthesis method [15-17].

In last decade, the extensive scientific research has been carried out in material science to develop new materials for energy saving appliance and environmental protection. However, its significance of industrialization of the combustion synthesis process is capitalized. Synthesis of the phosphors has become an attractive area of research in terms of their essential and practical applications in lighting industry and energy saving importance [3, 18]. The development of rare earth doped inorganic phosphors development is a widespread research area in general to produce a variety of inorganic compounds which exhibit photoluminescence and thermoluminescence properties [19, 20]. Generally, the phosphor materials are simple or complex materials doped with alkali-earth or rare-earth ions. Pyrophosphates and phosphate-based phosphors are promising materials that can widely use in research for light-emitting devices and imaging applications [21]. To get the fine tuning of emitting light from the lighting device, precise distribution of the doping ions inside the host crystal structure is needed. The crystallite size, surface morphology, doping concentrations, and lattice is to be maintained in a controlled manner [22]. The decay time and luminescent efficiency in emission spectra are the essential parameters for good quality phosphor, strongly depends on the surface morphology, particle shape, and size [23]. This kind of materials can be easily produced by combustion synthesis method. As a result, many materials synthesized by combustion method have potential applications in the area of optical, electrical and biological research fields for the development of optical switch, biomarker, laser, etc [24].

The rare-earth doped phosphors also prepared by different methods like solid-state reaction at high temperature, sol-gel method, etc. Solid state reaction method requires a high temperature and long-time heating repeated milling to purify the obtained material [25]. As a result, the degradation of the material takes place in terms of luminescence property and yield of the phosphor which weaken significantly [26]. Sol-gel method has also having drawback such that the obtained powders have small crystallinity that required post-heating treatment to attain improved high crystallinity at high temperatures, which increases the agglomeration of the material. The promising combustion method can be employed to a broad range of inorganic reagents for the synthesis of wide verity of functional materials. In combustion method varying the oxidizer flow rates, fuel and its amount, the flame temperature can be easily controlled and are essential parameters for determining obtained particle characteristics [27]. The particle size of the material can easily controlled by varying concentration of reagents. The complex compound particles can be prepared by combining different salts according to stoichiometric ratio [28].

### 2.2.2. Principle

Alves, et al. reported, *"Combustion method is based on the principle that once a reaction of reagents is initiated under heating, an exothermic reaction occurs that becomes self-sustaining within a certain time interval, resulting in a powder as final product. The exothermic reaction begins at the ignition temperature and generates a certain amount of heat that is manifested in the maximum temperature or temperature of combustion. Combustion synthesis has the advantage of rapidly producing fine and homogeneous powders. Since it is an exothermic, auto-propagated process, and with a high heat release rate, it can be explosive and should be undertaken with extra precautions*" [12, 29, 30].

### 2.2.3. Control Parameters of Combustion

The important control parameters in combustion method has been used to get desired material according to their applications. In the literature, several parameters like nature of flame, temperature variation, nature of atmosphere, chemical compositions of precursor, fuel-oxidant ratio and generated gases, etc are investigated [31].

#### 2.2.3.1. Precursor Use as Oxidants

Generally, nitrate salts are preferred as metal precursors because they are elementary oxidants require in the combustion method. Metal nitrates are used to provide the metal ion, and they have great water solubility that permit a better homogenization of oxidants [3]. Majority of oxide material were synthesized by combustion method, in which a metal nitrate and fuel were combined together. In some material synthesis, metal oxides and carbonates were used with dilute nitric acid according to their chemical composition and application of the materials. Nitrate groups ($NO_3$) of the oxidant act as oxidizing agents in combustion process [12]. Sometimes ammonium nitrate ($NH_4NO_3$) and nitric acid ($HNO_3$) are also used as an extra oxidant in combustion reactions which can not affect the percentage of the main participant of the chemical reaction [12].

#### 2.2.3.2. Fuel

The selection of fuel in combustion synthesis is based on certain criteria such as the fuel should have very good water solubility, low ignition temperature. During the combustion process, large amount of gases should be evolved. The reaction should not be volatile. It should be low cost and easily available. In view of such kind of characteristics, some organic fuels were selected in combustion method. The fuels employed are mainly hydrazine-based compounds such as urea, glycine, citric acid, sucrose, alanine, asparagine, serine, methyl cellulose, ammonium acetate, ammonium citrate and ammonium tartrate [32]. Out of all these fuels majority make available for two purposes, they provide large resource of C and H as result during combustion process. Huge amount of $CO_2$ and $H_2O$ generated with release of heat, and majority of them contains -$NH_2$ group and -COOH group which can provide desolation complexes of various metal ions and prevent their selective precipitation to maintain compositional homogeneity [33, 34].

Generally, after combustion process using different types of the organic fuels, desired materials can procured with particle size of micrometer and nanometer order. But in many cases, to obtain organic impurity free pure crystalline material, further calcination or annealing process is essentially required in synthesis process. Table 2.1 contain the basic information of some important fuels that are used in combustion method to synthesize different materials for various applications. In these present work, urea is used as fuel to prepare all the samples for luminescent phosphors.

| Fuel | Formula | Melting Point | Type | Applications |
|---|---|---|---|---|
| **Urea** | **$CH_4N_2O$** | **133 °C** | **Organic** | Materials for **Phosphors**, **Optical Materials**, Energy Technologies, Heterogeneous Catalysts, Semiconductors, Nano-ceramics, Bio-ceramics, etc. |
| Glycine | $C_2H_5NO_2$ | 233 °C | Organic | |
| Citric acid | $C_6H_8O_7$ | 153 °C | Organic | |
| Sucrose | $C_{12}H_{22}O_{11}$ | 186 °C | Organic | |
| Alanine | $C_3H_7NO_2$ | 258 °C | Organic | |
| Asparagine | $C_4H_8N_2O_3$ | 234 °C | Organic | |
| Serine | $C_3H_7NO_3$ | 246 °C | Organic | |
| Ammonium Acetate | $C_2H_7NO_2$ | 114 °C | Organic | |
| Ammonium Tartrate | $C_4H_{12}N_2O_6$ | Decomposes on heating | Organic | |

**Table 2.1** Basic information of fuels used in combustion synthesis method.

### 2.2.3.3. Composition of Precursor and Fuel-oxidant Ratio

Type of precursor and the quantity of precursor taken as per the balanced chemical reaction and the stoichiometric ratio affects the characteristics of the materials and its properties. Generally, the precursor of oxidant and fuel used in combustion synthesis should be water-soluble, otherwise, other solvents like ammonium nitrate ($NH_4NO_3$) and nitric acid ($HNO_3$) are added to increase the solubility of precursor. Use of water-soluble fuel is the necessity in combustion method. To obtain excellent product material with high homogeneity, the chemical precursors used in the process should be intimately mixed into the oxidants and fuels dissolved in water [12]. In the solution of mixtures of different oxidizers and fuel are broken down very fast via deflagration burning or combustion [35]. In some processes, the fuel also acts as a complexing agent that put a limit on the precipitation of the precursor before the firing. The inorganic salts used in combustion synthesis are usually low cost, highly water-soluble, high thermal stability at high temperatures and easy to remove from the final product mixture [12].

### 2.2.3.4. Oxidant-Fuel Ratio

In combustion synthesis method, the ratio of the oxidizer- fuel mixtures is one of the most important and essential thermo-chemical parameter for combustion. The principle of propellant chemistry and the element stoichiometric valances coefficient '$\phi$' is been used to calculate the stoichiometry of fuel to oxidant. This parameter is determined by using the total oxidizing and reducing valences of the oxidant-fuel elements, which serve as numerical coefficients for the stoichiometric balance [31, 36]. The ratio of oxidizer to fuel mixture is called a mixture ratio or equivalence ratio or elemental stoichiometric coefficient, etc. The fuel is mixed in precursor in such a way that the metal nitrate to fuel ratio can be preserved at the molecular level of complex [37]. To make proper combustion of material the oxidant-fuel ratio should be taken as unity that can be attained by selecting the suitable fuel and maintaining the initial solution concentration and ignition temperature constant [34]. The oxidant to fuel ratio should be varied from fuel deficient to fuel rich mixture which can be determined mode of propagation of combustion process and obtained powder properties [38]. The richness or leanness of fuel a combustible mixture is generally determined by the equivalence ratio '$\phi$', which is defined as $\phi = \phi_s / \phi_m$, where $\phi_m$ is the mixture ratio and $\phi_s$ is the stoichiometric ratio [39]. If value of '$\phi$' is greater than unity signify that the mixture is fuel lean, whereas '$\phi$' is less than unity shows that the mixture to be fuel rich. The value of '$\phi$' can defined the reaction taking place in mixture either slow and flameless reaction or explosive reaction throughout the volume and locally ignited reaction [40]. It is also found that a value of the equivalence ratio '$\phi$' may be differ significantly with respect to oxygen balance for the most part because the mixture ratio of the fuel-oxidizer elements does not take in count the intermolecular elements present in the oxidizer and in the fuel [41].

The oxidant-fuel molar ratio essential for the stoichiometric mixture is calculated by sum of the total oxidizing element valences and reducing element valences in the oxidizer, dividing by the sum of the total oxidizing element valences and reducing element valences in the fuel. The fuel to oxidant ratio is given by the equation below [39, 42],

$$\text{Oxidant} - \text{Fuel ratio} = \frac{\sum \text{oxidizing and reducing elements in oxidizer}}{(-1)\sum \text{oxidizing and reducing elements in fuel}}$$

In this calculation, only oxygen is taken as oxidizing element; carbon, hydrogen, and metal cation are taken as reducing elements; and nitrogen is neutral [42]. As well as making another consideration that oxidizing elements have positive valences and reducing elements have negative valences.

The material used as a fuel should be an organic composite that reliably capable of burning the carbon-hydrogen bonds (electrons acceptor). An oxidant is an oxygen-rich inorganic substance that can help in combustion and providing oxygen (electrons donor). To produce substantial heat through the exothermic reaction, the oxidizer and fuel are intimately mixed in a suitable proportion [43]. The reaction can starts in the oxidizer and fuel mixture at a certain temperature, called as the ignition temperature. The oxidizer to fuel ratio is one of the most essential parameter to signify the properties of synthesized powders [44]. The important properties of the powder material such as crystallite size, porosity, surface area, morphology, crystalline phase, degree and nature of agglomeration are usually controlled by adjusting proper ratio of oxidant-fuel [12, 45]. The pore size of particles are significantly depends on the fuel-oxidant ratio, as a result, the pore size is increased with increase in the amount of fuel.

#### 2.2.3.5. Atmosphere

The reaction atmosphere is a most important factor in combustion synthesis because the composition and the phase formation of material significantly depend on it [46]. The reaction atmosphere plays an important role that can affect the reaction kinetics and the phase composition of the material. The influence of surrounding environment and low reaction temperature can result in an incomplete combustion that can affect purity of material produced in this method [47]. To obtain high purity materials, the atmosphere should be selected in such a way that it can form a single material with least metastable phases. Majority of combustion processes is been completed in air at atmospheric pressure, sometimes nitrogen, oxygen and argon are used at different pressure are used as atmospheric agent [12]. According to literature, the atmospheric effect is weakly investigated parameter in combustion synthesis method.

#### 2.2.3.6. Nature of Flam of Combustion

The formation of the combustion flame arises through the release of heat from the chemical burning of the transformed substances. In combustion method controlled conditions, generates smoldering type of flame, depending on the employed fuel and oxidizer-fuel ratio [48, 49]. The generated burning flame during combustion can be sustain for seconds or even for minutes, during which the smoldering flame does not rise or it should be extinguished within a few seconds [12, 50]. The type of flame in the combustion plays an important role in controlling the particle size of as-synthesized powders [51]. In combustion process, the mixture of the fuel and oxidizer and the ignition can be controlled by an external sources [41]. These conditions are crucial for generating the flame. There is a dependency between the type of flames and the fuel used. It can be observed in the use of urea and a solution of glycine, where urea acts more reactive to the form the flame glow than glycine [3, 12, 52]. It can be characterized by smoldering. The nature of combustion process be influenced by the ligand groups present in the molecules of the fuel, as well as the compositional ratio of fuel and oxidant [48].

#### 2.2.3.7. Temperatures Variation in Combustion

There are various state taking place during the combustion in which temperatures variation occur that can have an effect on the reaction process as well as the properties of the final product.

***Initial Temperature*****:** It is the mean temperatures of the mixture of reagents before the reaction is go up in flames. ***Ignition Temperature*****:** It is the temperature of the point during combustion at which the combustion reaction is energetically triggered without any additional supply of external heat. ***Adiabatic Flame Temperature*****:** It is the maximum temperature attained under adiabatic environment during combustion. ***Maximum Flame Temperature*****:** It is the maximum temperature attained under conditions that are not adiabatic during combustion. ***Annealing Temperature*****:** It is the temperature above the recrystallization temperature to give the heating treatment to the material for enhances the chemical and physical properties of the material [11, 53, 54].

The flame temperatures are influenced by a large number of factors. The flame temperature can be increased with the addition of excess oxidant, such as nitrate ammonium, or the increase of the fuel-oxidant [12]. The adiabatic flame temperature can be calculated using the heat capacity of the products, the ignition temperature and the heat of combustion, assuming that no heat is lost in the system [55, 56]. The flame temperature measurements are almost always much smaller than the calculated adiabatic values, the real flame temperature can be decreased by some parameters such as radiation losses, incomplete combustion and air heating [12].

#### 2.2.3.8. Gas Generation

The properties of the material synthesized by combustion synthesis method such as the morphology of material, particle size, smoothness of the surface, porosity, shape of particles are mainly affected by the gas generated during combustion and the atmosphere provided for the combustion [50, 52]. The variation of particle size by the use of different fuel depends on the amount of gas generated during combustion and the generation of gas depends on the fuel-oxidant ratio [34]. The large amount of gas generated in combustion can break large clusters of molecules which can raise the pore formation between the particles [57]. As a result, the disintegration of the clusters takes place and suddenly more amount of heat generates from the material which can hindering the particle growth.

### 2.2.4. Scope of Combustion Synthesis

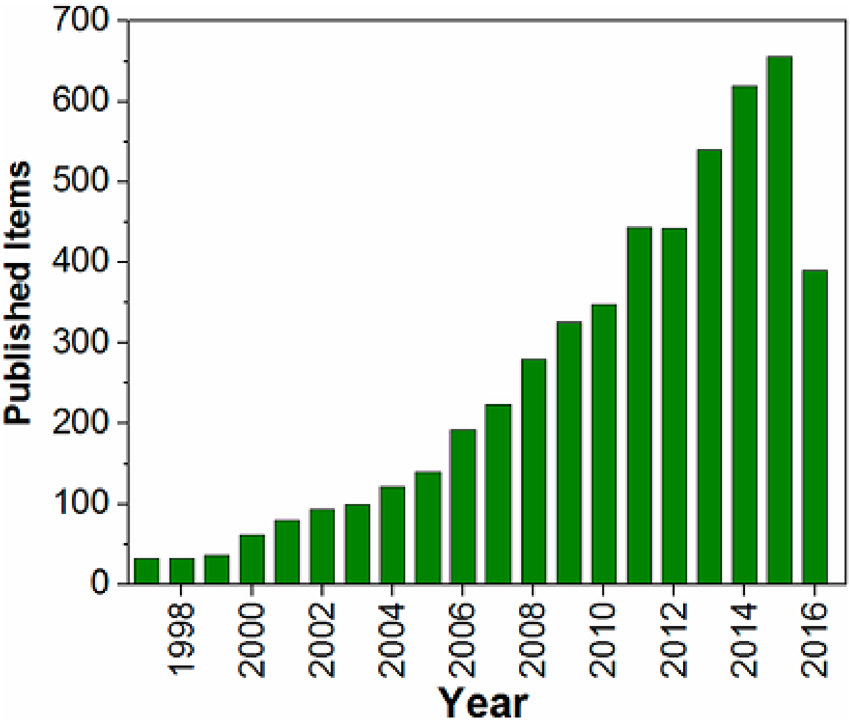

**Figure 2.1** Published articles in each year according to Web of Science, August 2016 [3].

The recent research in material science and solid state physics for the development of novel materials with unique structures and unusual properties is based on combustion synthesis method. Figure 2.1 shows the research papers published in each year on the basis of combustion synthesis [3]. It represents, how combustion synthesis method developed each year in the field of material science.

Brief information of the scope of the materials developed by combustion method for versatile application is discussed below:

***Materials for energy application*:** The materials for energy storage device and energy generating devices, like batteries, super-capacitors, fuel cells, and solar cells were developed by combustion method. Desired characteristics of the materials require for energy storage devices such as high efficiency and high energy storage capacity is achieved due to the excellent properties of material.

***Heterogeneous catalysts*:** In-depth analysis of relations between combustion characteristics and performance of combustion method catalysts are identified. Specific issues related to combustion method, derived catalysts are addressed in the context of important catalytic reactions, including hydrocarbon reforming, oxidation, and automotive/diesel exhaust emissions treatments.

***Semiconductors and optical materials*:** Many research papers have been published on the prospect of synthesis and characterization of semiconducting and optical materials for the development of optical devices in solid state lighting. Strategies and principles to doped semiconducting materials for tuning the light-emitting behavior are outlined.

***Thin-films*:** The use of combustion method in nanomaterial for development of large-area, low-cost thin film transistors and other devices is discussed. Specific features and prospects of low-temperature combustion method in the development of thin films are considered.

***Nano-ceramics*:** Recent developments in design, synthesis, characterization, and applications of nanostructured functional ceramic materials are summarized. Specifically, recent trends in combustion processing of electro-, magnetic- and bio-ceramics are outlined.

## 2.3. Materials And Sample Preparation Method

Commercially purchased pure analytical reagent grade precursors such as strontium carbonate, ammonium dihydrogen phosphate, cerium oxide, europium oxide, dysprosium oxide, terbium oxide, gadolinium oxide, erbium oxide, and samarium oxide were used for the synthesis of rare earth doped strontium pyrophosphate. Urea was used as a fuel for combustion in this method. The list of samples synthesized for $Re^{3+}$ doped and co-doped $Sr_2P_2O_7$ phosphors are summarized in Table 2.1 and Table 2.2 respectively. Figure 2.2 shows the different steps of combustion synthesis method adopted for synthesis of rare earth doped $Sr_2P_2O_7$. In this method, different steps involved such as formation of mixture of precursors, grinding, heating treatment and grinding of obtained material after heating. The balanced chemical reaction for the synthesized phosphor is given below,

$$2\,SrCO_3 + 2\,(NH_4)_2HPO_4 \rightarrow Sr_2P_2O_7 + 3\,H_2O + 2\,CO_2 + 4\,NH_3$$

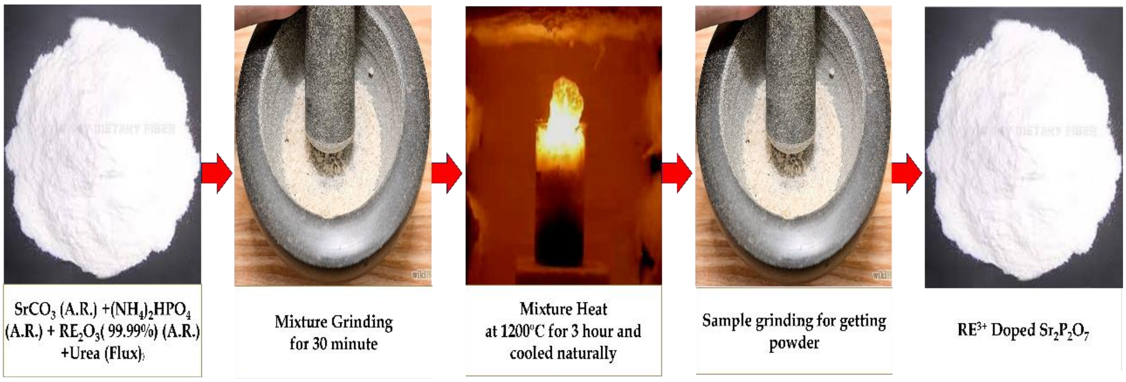

**Figure 2.2** Different steps of combustion synthesis method adopted for synthesis of rare earth doped $Sr_2P_2O_7$.

| Sample | Doping Ion Concentration (mol%) |
|---|---|
| $Sr_2P_2O_7$: x $Ce^{3+}$ | x = 0.5, 1.0, 1.5, 2.0, 2.5 |
| $Sr_2P_2O_7$: x $Eu^{3+}$ | x = 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 |
| $Sr_2P_2O_7$: x $Tb^{3+}$ | x = 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 |
| $Sr_2P_2O_7$: x $Dy^{3+}$ | x = 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 |
| $Sr_2P_2O_7$: x $Er^{3+}$ | x = 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 |
| $Sr_2P_2O_7$: x $Gd^{3+}$ | x = 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 |

**Table 2.1** List of sample of single $RE^{3+}$ doped $Sr_2P_2O_7$ synthesized for the study of its luminescence properties.

| Sample | Doping Ion Concentration (mol%) |
|---|---|
| $Sr_2P_2O_7$: x $Ce^{3+}$, y $Eu^{3+}$ | x = 1.0, y = 1.0 |
| $Sr_2P_2O_7$:x $Ce^{3+}$, y $Tb^{3+}$ | x = 1.0, y = 1.0 |
| $Sr_2P_2O_7$: x $Ce^{3+}$, y $Dy^{3+}$ | x = 1.0, y = 1.0 |
| $Sr_2P_2O_7$: x $Ce^{3+}$, y $Er^{3+}$ | x = 1.0, y = 1.0 |
| $Sr_2P_2O_7$: x $Ce^{3+}$, y $Gd^{3+}$ | x = 1.0, y = 1.0 |
| $Sr_2P_2O_7$: x $Ce^{3+}$, y $Sm^{3+}$ | x = 1.0, y = 1.0 |
| $Sr_2P_2O_7$: x $Ce^{3+}$, y $Nd^{3+}$ | x = 1.0, y = 1.0 |

**Table 2.2** List of sample of double rare earth doped $Sr_2P_2O_7$ synthesized for the study of its luminescence properties.

## 2.4. Rare Earth Doped Strontium Pyrophosphate

### 2.4.1. $Sr_2P_2O_7$: $Ce^{3+}$

$Ce^{3+}$-doped $Sr_2P_2O_7$ phosphors were synthesized by the combustion method for different concentrations namely 0.5, 1.0, 1.5, 2.0 and 2.5 mol%. The phosphors were synthesized from the precursors $SrCO_3$ (A.R.), $(NH_4)_2HPO_4$ (A.R.), $Ce_2O_3$ (99.99%) (A.R.) and urea. The precursors were taken as per the stoichiometric ratio considered from the balanced chemical equation. Urea was used as a fuel at a ratio 15% of the total mass of the mass of precursors. The precursors were ground in mortar pastel for 30 minute to obtain homogeneous mixture. The homogeneous mixture was transferred into alumina crucible and put inside the muffle furnace for heat treatment at 1200°C for 3 hour at atmospheric pressure. After heating treatment, the furnace was allowed to cool naturally to the room temperature. All prepared samples were in the pure white powder form. The samples were ground in a mortar–pestle for half hour to obtain the homogeneous fine powder form [58].

### 2.4.2. $Sr_2P_2O_7$: $Eu^{3+}$

$Eu^{3+}$-doped $Sr_2P_2O_7$ phosphors were synthesized by the combustion method for different concentrations namely 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 mol%. The phosphors were synthesized from the precursors $SrCO_3$ (A.R.), $(NH_4)_2HPO_4$ (A.R.),

$Eu_2O_3$ (99.99%) (A.R.) and urea. Further process followed for the synthesis of series of $Eu^{3+}$-doped $Sr_2P_2O_7$ similar to that of the process explained in Section 2.4.1 [59].

### 2.4.3. $Sr_2P_2O_7$: $Tb^{3+}$

$Tb^{3+}$-doped $Sr_2P_2O_7$ phosphors were synthesized by the combustion method for different concentrations namely 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 mol%. The phosphors were synthesized from the precursors $SrCO_3$ (A.R.), $(NH_4)_2HPO_4$ (A.R.), $Tb_2O_3$ (99.99%) (A.R.) and urea. Further process followed for the synthesis of series of $Tb^{3+}$-doped $Sr_2P_2O_7$ similar to that of the process explained in Section 2.4.1 [60].

### 2.4.4. $Sr_2P_2O_7$: $Dy^{3+}$

$Dy^{3+}$-doped $Sr_2P_2O_7$ phosphors were synthesized by the combustion method for different concentrations namely 0.5, 1.0, 1.5, 2.0 and 2.5 mol%. The phosphors were synthesized from the precursors $SrCO_3$ (A.R.), $(NH_4)_2HPO_4$ (A.R.), $Dy_2O_3$ (99.99%) (A.R.) and urea. Further process followed for the synthesis of series of $Dy^{3+}$-doped $Sr_2P_2O_7$ similar to that of the process explained in Section 2.4.1.

### 2.4.5. $Sr_2P_2O_7$: $Er^{3+}$

$Er^{3+}$-doped $Sr_2P_2O_7$ phosphors were synthesized by the combustion method for different concentrations namely 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 mol%. The phosphors were synthesized from the precursors $SrCO_3$ (A.R.), $(NH_4)_2HPO_4$ (A.R.), $Er_2O_3$ (99.99%) (A.R.) and urea. Further process followed for the synthesis of series of $Er^{3+}$-doped $Sr_2P_2O_7$ similar to that of the process explained in Section 2.4.1 [61].

### 2.4.6. $Sr_2P_2O_7$: $Gd^{3+}$

$Gd^{3+}$-doped $Sr_2P_2O_7$ phosphors were synthesized by the combustion method for different concentrations namely 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 mol%. The phosphors were synthesized from the precursors $SrCO_3$ (A.R.), $(NH_4)_2HPO_4$ (A.R.), $Gd_2O_3$ (99.99%) (A.R.) and urea. Further process followed for the synthesis of series of $Gd^{3+}$-doped $Sr_2P_2O_7$ similar to that of the process explained in Section 2.4.1.

## 2.5. Rare Earth Co-Doped Strontium Pyrophosphate

### 2.5.1. $Sr_2P_2O_7$: $Ce^{3+}$, $RE^{3+}$

The phosphors $Sr_2P_2O_7$: 0.1 mol% $Ce^{3+}$, 0.1 mol% RE (RE = $Eu^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Er^{3+}$, $Sm^{3+}$, $Gd^{3+}$, $Nd^{3+}$ ) were synthesized by complex combustion method at 1200°C. Combustion synthesis method is termed as a fast exothermic reaction that liberates large amount of energy in the form of heat and flames. The combustion process results of time-dependent thermodynamic events which can takes place at particular temperature depends on the fuel used for the combustion. It can occurs on a molecular level that can produce annihilation and rearrangement of certain molecules, atoms, radicals, and solid boundaries. The host $S_2P_2O_7$ (Strontium Pyrophosphate) was doped with $Ce^{3+}$ ion and co-doped with different trivalent rare earth ions. The precursors $SrCO_3$, $NH_4H_2PO_4$, $Ce_2O_3$, $Eu_2O_3$, $Tb_2O_3$, $Dy_2O_3$, $Er_2O_3$, $Sm_2O_3$, $Gd_2O_3$, and $Nd_2O_3$ were taken as per the stoichiometric ratio according to the chemical equation balancing. In this method, all precursor were purchased highly purified analytical research graded materials which can used further without purification. Ten percent of the total mass of the mixture of precursor, urea is taken as combustion fuel. The precursors were ground in mortar pastel for 30 minute to obtain homogeneous mixture. The homogeneous mixture was transferred into an alumina crucible and placed in a muffle furnace in air for heating at 1200°C for three hour. After the heating process, the samples were allowed to cool naturally to the room temperature. All prepared samples were in the pure white powder form. The samples were ground in a mortar–pestle for half hour to obtain the homogeneous fine powder form [58, 60, 62].

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