Chapter 3

Synthesis Techniques

3.1 Ceramic Method

The most widely used method for the preparation of polycrystalline solids (i.e. powders) is the direct reaction of a mixture of solid starting materials in the solid state [1, 2]. The starting materials are usually salts of individual constituents which are mechanically mixed using mortar and pestle or a planetary mill. Homogenization of the mixture is aided greatly by adding sufficient quantity of a volatile organic liquid such as acetone or alcohol to form slurry. During the process of grinding and mixing, the organic liquid gradually volatilizes and is evaporated completely at the end of the operation. Solids do not usually react together at room temperature over normal timescales and it is necessary to heat them to much higher temperatures, often 1000 to 1500°C, for the reaction to occur at an appreciable rate. This shows that both the thermodynamic and kinetic factors are important in solid state reactions: thermodynamic considerations show whether or not a particular reaction should occur, taking into consideration the changes in free energy that are involved; kinetic factors determine the rate at which the reaction occurs. Hence, the homogenized mixture is then fired at high temperature in a suitable container such as platinum crucible, alumina crucible, etc which are chemically inert to the reactants under the heating conditions used. The first step of the reaction must be the decomposition of the salts and the mixture should be heated first at an appropriate temperature for a few hours so that decomposition occurs in a controlled manner. Reaction to give final product usually requires several hours, or even days, depending upon the reaction rate at a given temperature. Solid-solid reaction is often greatly facilitated by cooling and grinding the sample periodically, This is because during heating, sintering and grain growth of both reactant and product phases usually occur in addition to the main reaction, causing a reduction in the surface area of the mixture. The effect of grinding is to maintain a high surface area, as well as to bring fresh surfaces into contact. In the solid state, the reaction is diffusion controlled; hence higher temperature is necessary for enhanced diffusion rates so that the reaction proceeds faster. At lower temperatures very long time is required for the formation of the phase pure product. Solid-state reactions have some disadvantages:

1. Improper mixing of the reactants results in incomplete reactions. As a result, the desirable parameters e. g. the emission efficiency will come down. If any of the unreacted reactants, say, metal oxides has an absorption band in the visible region, it manifests itself in absorption of the overlapping emission bands.

2. The products are likely to be contaminated by the planetary mill on repeated use for different compounds.

3. Homogeneous distribution of the dopant is not possible in the host matrix. This results once again in factors like reduced emission intensity. The dopants should not be segregated in a given part of the product, as it results in self quenching of luminescence.

4. Because of high firing temperatures, partial loss of volatile reactants may result in non-stoichiometric compounds. Further, high firing temperature causes the increase of the production costs.

5. The particle size distribution is large and often results in aggregates. However, a good product e. g. phosphor for lighting or display applications needs the uniform distribution of particle size.

3.2 Combustion Synthesis

Synthesis of oxide phosphors has been achieved by a variety of routes: solid-state reactions [3, 4], sol–gel techniques [5], hydroxide precipitation [6], hydrothermal synthesis [7, 8] and combustion synthesis [9–11]. Solid-state reactions are performed at high temperatures, typically around 1600°C, because of the refractory nature of the oxide precursors. For multi element compositions, an incomplete reaction is often obtained with undesirable precursor products present in the final product. Therefore the formation of solids by ceramic method requires repeated grinding, pelletizing and calcination of reactants for longer durations at high temperatures to control the diffusion of atoms and ionic species through reactants and products. For sol–gel and hydroxide precipitation methods, dilute solutions of metallorganics or metal salts are reacted and condensed into an amorphous or weakly crystalline mass. The advantage of these methods is that atomically mixed powders are obtained in the as synthesized condition and problems associated with incomplete reactions are avoided. However, these as-synthesized materials must also be heat treated to high temperatures to crystallize the desired phase and to achieve particle sizes greater than 0.2 μm. Hydrothermal synthesis is a low temperature and high pressure decomposition technique that produces fine, well-crystallized powders [8]. These powders must also be heat treated to high temperature to extract the maximum luminous efficiency. 'Combustion synthesis' also known as fire or furnaceless synthesis is one such approach. It has emerged as an important technique for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, intermetallics and nanomaterials [12]. The process makes use of highly exothermic redox chemical reactions between metals and non metals, the metathetical (exchange) reaction between reactive compounds or reactions involving redox compounds/mixtures. Depending upon the nature of reactants: elements or compounds (solid, liquid or gas); and the exothermicity (adiabatic temperature, T_{ad}), Combustion Synthesis is described as: 'self-propagating high-temperature synthesis' (SHS); low-temperature combustion synthesis (LCS), solution combustion synthesis (SCS), gel-combustion, sol–gel combustion, emulsion combustion, volume combustion (thermal explosion), etc. The term 'combustion' covers flaming (gas-phase), smouldering (heterogeneous) as well as explosive reactions and the process is characterized by high-temperatures, fast heating rates and short reaction times. These features make Combustion Synthesis an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. Some other advantages of Combustion Synthesis are:

i. Use of relatively simple equipment
ii. Formation of high-purity products
iii. Stabilization of metastable phases and
iv. Formation of virtually any size and shape products

The combustion method has been successfully used in the preparation of a large number of technologically useful oxide (refractory oxides, magnetic, dielectric, semiconducting, insulators, catalysts, sensors, phosphors etc.) and non oxide (carbides, borides, silicides, nitrides etc.) materials. More than 500 materials have been synthesized by this process, many of which are commercially manufactured in Russia. There is tremendous interest in the combustion synthesis of materials because it is simple, fast, energetically economic and yields high purity products compared to the conventional routes used to prepare these materials. As it is a high-temperature process, only thermodynamically stable phases can be prepared. At the same time, rapid heating and cooling rates provide the potential for the production of metastable materials with new and unique properties.

Merzhanov, one of the pioneers of SHS has periodically reviewed [13] the developments in SHS and its applications. A quarterly journal, 'International Journal of Self-Propagating High-Temperature Synthesis' devoted to SHS has been published by Allerton Press Inc; New York, since 1992 with Alexander G Merzhanov as the 'General Editor'. Four International Symposia on SHS have been held, in 1991 (Alma-Ata, Kazakhstan), 1993 (Honolulu, USA), 1995 (Wuhan, China) and 1997(Spain). Here four different approaches of combustion synthesis viz. SHS, Solid State Metathesis (SSM), Gas phase synthesis and Solution Combustion Synthesis (SCS) are discussed below.

Self Propagating High Temperature Synthesis (SHS) and related Processes

Materials like borides, carbides, nitrides, silicides, ceramics, intermetallics, composites and oxides can be synthesized by SHS process. Here the initial reactants, intermediates and final products are all in the solid state.The reactants are pressed into a pellet, typically cylindrical in shape. The pellet is then ignited by an external source (e.g. tungsten coil, laser or microwave) either locally (SHS) or uniformly (VCS), which initiates an exothermic reaction. For SHS, the reaction should be highly exothermic (ΔH~40 kcal mol^{-1} or 16 800 J mol^{-1}) and the rate of heat generation must be greater than the heat dissipated, otherwise the reaction will be quenched and will not be self-propagating. After the ignition the combustion reaction is self propagating with an adiabatic temperature in the range of 1500-3000K. The high ignition temperature (1500°C) required, can be attained by laser radiation, a resistance heating coil, an electric arc, a chemical oven and so on. Innovations in SHS processes are aimed at lowering the ignition temperature and using metal oxides/halides instead of finely divided metal powders. To lower the ignition temperature, mechanical activation and field activation processes are used. Field activated combustion synthesis has been used by Munir and co-workers [14] to activate low enthalpy of formation (e.g. Silicon Carbides, Boron Carbide, Tungsten Carbide, Tungsten disilicide etc.) reactions. Rate of the combustion reaction increases with the application of a magnetic field and the magnetic properties of the products also improve. The main limitations of Field Activated Combustion Synthesis is that the process cannot be used for reactions that form materials with high conductivity as the current density in the heating zone decreases leading to extinction of the wave.

Gravity significantly influences the Combustion Synthesis and more uniform microstructured products are formed [15]. This also opens the possibility of production of nanophase materials with high porosity. Microgravity leads to decrease in average particle size and overall decrease in microstructural transformation rates.

Thermite reactions which involve metallo-thermic reduction have been employed in the ceramic coating of pipes as well as in the preparation of composites. There are two types of thermite reactions. The first method involves the reduction of an oxide to the element. The second type of thermite process involves the reduction of an oxide to the element which subsequently reacts with another element to form a refractory compound [16]. The advantages of SHS process are time and energy savings and an increase in the reactivity of the products.

Solid State Metathesis (SSM)

Unlike the SHS reactions (elemental or thermite reactions) which employ metals, nonmetals and oxides, this method involves rapid, low temperature initiated solid-state exchange reactions between reactive metal halides with alkali metal main group compounds [17]. The exothermicity of the reaction reaches nearly 1050°C within =300ms. A generalized reaction scheme is ignite

$MX_{m}, + mAY_{n}, \rightarrow MY_{z} + mAX + [(m,n) - Z]\ Y$

Where M= metal, X= halide, A=alkali metal and
Y = nonmetal or metalloid m, n = no. of moles.

The SSM reactions can be initiated either by simply mixing/grinding or by a hot filament. Once the SSM reaction is initiated, it becomes rapidly self-sustaining and can reach high temperatures (>1000°C) within a short period (<2s). Initiation generally occurs when one of the precursors changes phase or decomposes enabling increased surface contact. A number of technologically important materials for example, superconductors (NbN, ZrN), semiconductors (GaAs, InSb), insulators (BN, ZrO_2), magnetic materials (GdP, SmAs), chalcogenides (MoS_2, NiS_2), intermetallics ($MoSi_2$, WSi_2), pnictides(ZrP, NbAs), and oxides (Cr_2O_3) have been prepared by an SSM reaction. Formation of high-temperature cubic/tetragonal ZrO_2 and β-$MoSi_2$ is reported by this process.

Gas Phase Synthesis

Flame synthesis differs from the typical SHS process in that all reactions take place in the gas-phase and form fine powders (often nanoscale as in carbon soot from HC flames, fumed silica, titania etc.). The possible advantages of this process over normal solid/solid, solid/liquid, SHS processes are its continuous rather than batch process of the latter and the higher purities of the products. Many high purity materials can be synthesized by self-sustaining gas-phase reactions. It is well known that metal halides react spontaneously when their vapours are brought into contact with gaseous or liquid reactive metals such as sodium or magnesium [18].

Such gas-phase combustion or flame synthesis has been used to prepare fine particle metal nitrides (Si_3N_4), carbides (SiC, B_4C, TaC), borides (TiB_2, ZrB_2), silicides ($TiSi_2$), photovoltaic silicon, advanced fuels and refractory metals (Ti, Ta, Zr, Hf, and Nb).

Nanosize silica, titania, alumina and tialite (Al_2TiO_5) have been prepared by flame synthesis using the corresponding metal halides and H_2/air or HC/air flames.

High surface area SiO_2 having nanosize particles are prepared by the addition of ferrocene to $SiCl_4$ [19]. TiB_2 Nanoparticle (unagglomerated) has been obtained by the addition of NaCl [20]. Flame synthesis has also been used to prepare nanosize SiC [21] and TiB_2 [20].

Solution Combustion Synthesis

An entirely different approach to the synthesis of simple and complex oxide materials is presented. This approach involves the use of novel combustible precursors (redox compounds) and redox mixtures. It uses low temperature (<5OO°C) initiated gas-producing exothermic reactions which are self-propagating and yield voluminous fine particle oxides in few minutes. Compounds like $(NH_4)_2Cr_2O_7$ which contain both oxidizing ($Cr_2O_7^{2-}$) and reducing (NH_4^+) groups when properly ignited (using $KClO_3$-sucrose-H_2SO_4) decompose autocatalytically to yield voluminous green Cr_2O_3 [22].

The exothermicity of the combustion reaction is due to the oxidation of NH_4^+ to N_2 and H_2O by the dichromate ion which itself is reduced to Cr^{3+}. The combustion is smouldering type (flameless) and is accompanied by the evolution of gases resulting in fine, voluminous Cr_2O_3 powder.

A new class of precursors containing a carboxylate anion, hydrazide, hydrazine or hydrazinium groups were accidentally found to ignite at low temperature (120-350°C) and decompose autocatalytically to yield fine particle, large surface area oxides [23]. The high exothermicity (T_{ad} =lOOO°K) of combustion was attributed to the oxidation of strong reducing molecules such as COO^-, $N_2H_3^-$, N_2H_4 or $N_2H_5^+$ (present in the precursors) by atmospheric oxygen to CO_2, H_2O and N_2. Other nanosize oxides obtained by the combustible precursors are CeO_2, TiO_2 and Y_2O_3. Besides magnetic oxides a few ferroelectric titanates have also been prepared by this route. Fine particle γ-Fe_2O_3, Fe_3O_4 and ferrites find use as recording materials and in the preparation of liquid magnets. Titania, ferrites and cobaltites are all good catalysts.

Although the preparation of fine particle oxide materials by the combustion of redox compounds is simple and attractive, it has certain limitations. Firstly, the preparation of the precursors requires several days. Secondly the yield is only about 20% of the precursor. Finally, not all metals form complexes with the hydrazine carboxylate ligand and therefore it is not possible to use this method to prepare high-temperature oxides like chromites, alumina and so on.

Furnace Combustion

An alternative method to the combustible redox compounds is the use of the redox mixtures (oxidizer-fuel) like gun powder (Potassium nitrate + Carbon + Sulphur) or solid propellant (NH_4ClO_4+CTPB+Al) which when ignited undergo self propagating combustion [24]. Oxide materials with desired composition and structures are prepared by rapidly heating aqueous solutions containing stoichiometric amounts of respective metal nitrate (oxidiser) and fuels like urea / hydrazides (carbohydrazide (CH), oxalyl dihydrazide (ODH), malonic acid dihydrazide (MDH), tetra formal tris azine (TFTA), etc.). The combustion reaction is initiated in a muffle furnace or on a hot plate at temperatures of 500°C or less; much lower than the phase transition of the target material. In a typical reaction, the precursor mixture of water, metal nitrates, and fuel decomposes, dehydrates, and ruptures into a flame after about 3–5 min. The resultant product is a voluminous, foamy powder which occupies the entire volume of the reaction vessel. The chemical energy released from the exothermic reaction between the metal nitrates and fuel can rapidly heat the system to high temperatures (>1600°C) without an external heat source. Combustion synthesized powders are generally more homogeneous, have fewer impurities, and have higher surface areas than powders prepared by conventional solid-state methods [25].

Figure 1 *Cylindrical furnace*

The mechanism of the combustion reaction is quite complex. The parameters that influence the reaction include: type of fuel, fuel to oxidizer ratio, use of excess or less oxidizer, ignition temperature, and water content of the precursor mixture. The formation of the viscous liquid or gel is a primary condition for an intimate blending of the starting constituents and preventing the random redox reaction between a fuel and an oxidizer. The nature of the fuel, its amount and pH of the starting solution are some of the important process parameters for getting the transparent viscous gel without any phase separation or precipitation. In general, a good fuel should react non-violently, produce non-toxic gases, and act as a complexant for metal cations [25]. Complexes increase the solubility of metal cations, thereby preventing preferential crystallization as the water in the precursor solution evaporates [26]. It should be able to maintain the compositional homogeneity among the constituents and get combusted with an oxidizer at a low ignition temperature. Mainly two events occur during the combustion

(i) Flame Temperature or generation of heat of combustion and

(ii) Gas evolution.

The adiabatic flame temperature, T_f of the reaction is influenced by the type of fuel, fuel to oxidizer ratio, and the amount of water remaining in the precursor solution at the ignition temperature [27]. The flame temperature can be increased with the addition of excess oxidizer such as ammonium nitrate [25], or by increasing the fuel/oxidizer molar ratio. The following equation can be used to approximate the adiabatic flame temperature for a combustion reaction:

$$T_f = T_0 + \frac{\Delta H_r - \Delta H_p}{C_p}$$

where ΔH_r and ΔH_p are the enthalpies of formation of the reactants and products, respectively, C_p is the heat capacity of products at constant pressure, and T_0 is 298 K. Measured flame temperatures are typically lower than calculated values of flame temperature as a result of heat loss. Heat of combustion (or flame temperature) helps in crystallization and formation of the desired phase. However, very high flame temperature can affect the powder characteristics adversely like increase in the crystallite size, formation of hard agglomerates, and thereby reduction in the surface area and sinterability.

When complete combustion occurs, the only gaseous products obtained are N_2, CO_2, and H_2O, making this an environmentally clean processing technique. The evolution of gaseous products during the combustion dissipates the heat of combustion and limits the rise of temperature, thus reducing the possibility of premature local partial sintering among the primary particles. The difference in particle size with the use of different fuels depends upon the number of moles of gaseous products released during combustion. As more gases are liberated, the agglomerates are disintegrated and more heat is carried from the system thereby hindering particle growth. The gas evolution also helps in limiting the interparticle contact and hence resulting in more easily friable product with a very high surface area by creating micro and nanoporous regions. The powder characteristics like particle size, surface area, extent and nature of agglomeration (hard or soft) are primarily governed by enthalpy or flame temperature generated during combustion and gas evolution, which itself is dependent on nature of the fuel and fuel-to-oxidant ratio.

According to the principle of propellant chemistry, the stoichiometry of fuel to oxidizer mixture is usually expressed in terms of "elemental stoichiometric coefficient" ϕ_e a parameter which describes the relationship between intramolecular fuel and oxidizer [11]. It actually represents the ratio of oxidizing to reducing elemental composition. All the oxidizing and reducing elements are treated in a similar manner irrespective of whether they are present in oxidizer or fuel components. ϕ_e is defined as

$$\phi_e = \frac{\text{Total composition of oxidizing elements}}{\text{Total composition of reducing elements in the mixture}}$$

$$\phi_e = \frac{\Sigma(\text{Coefficient of oxidizing elements in specific formula}) \times (\text{valency})}{(-1)\Sigma(\text{Coefficient of reducing elements in specific formula}) \times (\text{valency})}$$

A mixture is fuel rich if $\phi_e < 1$, fuel lean if $\phi_e > 1$ and stoichiometrically balanced at $\phi_e = 1$. Stoichiometric mixtures are reported to produce maximum energy in propellant systems. The oxidizer to fuel molar ratio required for the stoichiometric mixture ($\phi_e = 1$) is determined by summing the total oxidizing and reducing valencies in the oxidizer compounds and dividing by the sum of total oxidizing and reducing valencies in the fuel compounds. The elements Hydrogen, Carbon and all metal elements are considered as reducing elements. with valencies +1 for Hydrogen, +4 for Carbon and corresponding valency for metal ion in that compound. Element Oxygen is considered to be as the only oxidizing element with valency -2. Nitrogen is considered to be neutral and the valency is taken as 0. For the purpose of calculating fuel to oxidizer ratio, the valencies of oxidizing elements are treated as positive and those of reducing elements are treated as negative.

The fuel to oxidizer ratio for $BaMgAl_{10}O_{27}$ (BAM) can be calculated as under

<u>Metal Nitrates (oxidizers)</u>	<u>Fuel</u>
$Ba(NO_3)_2$	Urea (CH_4N_2O)
$Mg(NO_3)_2$	
$Al(NO_3)_3$	

$$\frac{\frac{1}{12}[(1Ba\times-2)+(2N\times0)+(6O\times2)]+\frac{1}{12}[1Mg\times-2)+(2N\times0)+(6O\times2)]+\frac{10}{12}[(1Al\times-3)+(3N\times0)+(9O\times2)]}{(-1)[(1C\times-4)+(4H\times-1)+(2N\times0)+(1O\times2)]}$$

$$=\frac{170}{72}=2.36$$

So the ratio of metal nitrate to Urea is 2.36. This ratio is needed for $\phi_e = 1$, which implies complete combustion of all components.

Alternatively, the elemental stoichiometric coefficient ϕ_e is calculated as follows;

In $BaMgAl_{10}O_{27}$ the mole percent of Barium is 8.33, mole percent of Magnesium is 8.33 and mole percent of Aluminium is 83.33. The metal nitrates can be expressed as,

$Ba_{1\times0.0833}N_{2\times0.0833}O_{6\times0.0833} = Ba_{0.0833}N_{0.166}O_{0.5}$

$Mg_{1\times0.0833}N_{2\times0.0833}O_{6\times0.0833} = Mg_{0.0833}N_{0.166}O_{0.5}$

$Al_{1\times0.833}N_{3\times0.833}O_{9\times0.833} = Al_{0.833}N_{2.5}O_{7.5}$

Given a fuel to oxidizer ratio of r, the components of Urea can be expressed as,

$C_{1\times r}H_{4\times r}N_{2\times r}O_{1\times r} = C_{1r}H_{4r}N_{2r}O_{1r}$

Then, ϕ_e is calculated by

$$\phi_e = \frac{\Sigma(\text{all oxidizing elements in each of the three oxidizers and one fuel})}{(-1)\Sigma\ (\text{all reducing elements in each of the two oxidizers and one fuel})}$$

Substituting the values for Barium, Magnesium and Aluminium nitrates with urea as fuel,

$$\phi_e = \frac{(0.5\times2)+(0.5\times2)+(7.5\times2)+(r\times2)}{(-1)[(0.0833\times-2)+(0.0833\times-2)+(0.833\times-3)+(r\times-4)+(r\times-4)]} = \frac{17+2r}{2.8+8r}$$

For stoichiometric mixtures $\phi_e = 1$ so, $17+2r = 2.8 + 8r$,

Therefore, $r = 2.36$ which is in conformity with the fuel to oxidizer ratio calculated above.

There are several reports to optimize the processing parameters in combustion reactions to obtain powders with large surface areas. Hong. *et al.* [28] found that the batch water content affected the specific surface area of as synthesized powders. As the amount of water increased in the precursor mixture, the specific surface area also increased, since less heat was available for particle growth, as some of the heat is expended for the vaporization of water. Minimum precursor water content (0.667 ml/gm of nitrate) is required for complete atomic mixing and to prevent selective crystallization. It was also found that increase in furnace temperature resulted in decrease in specific surface area of as synthesized powder. Venkatachari et al.[29] in studies of combustion synthesized Zirconia powders found that at temperatures of 250°C and less precursor mixture of metal nitrate and fuel did not react. Furnace temperature was also found to strongly influence the specific surface are of as reacted powders. Contrary to the finding of Hong et al., [28] the specific surface area of the powder increased as the furnace temperature increased.

A wide range of technologically useful oxides (alumina to zirconia) were prepared with interesting dielectric, electrical, mechanical, catalytic, luminescent and optical properties. It was possible to prepare oxide materials with desired composition, structure (spinel, perovskite, garnets etc.) by solution combustion. Interestingly, some of the fuels used were found to be specific for a particular class of oxides e.g. urea—for alumina and related oxides; Carbohydrazide—for Zirconia and related oxides; Oxalyl dihydrazide—for Fe_2O_3 and ferrites, Tetra Formal Tris Azine—for TiO_2 and related oxides; glycine—for chromium manganites, chromites and related oxides, etc.

All these fuels serve two purposes

a. They are the source of Carbon and Hydrogen, which on combustion form CO_2 and H_2O and liberate heat.

b. They form complexes with the metal ions facilitating homogeneous mixing of the cations in solution.

The exothermicity (T_{ad}) of the redox reaction varies the temperature between 1000 and 1800 K. Depending upon the fuel used, the nature of combustion differs from flaming to non-flaming (smouldering). Not surprisingly, urea occupies the centre stage, probably due to its ready availability and high exothermicity. The ease of doping metal ions in oxide results into the facile synthesis of metal and alloy doped alumina, aluminates [30], pigments [31] and phosphors [32].

A variety of ceria and ceria-based oxide materials have been prepared by the Solution Combustion method using Oxalyl dihydrazide fuel [33, 34]. Another important application of Solution Combustion is in the preparation of Solid Oxide Fuel Cell (SOFC) materials. The solution combustion method not only yields nanosize TiO_2 [35], ZrO_2 [36] and hexaferrites [37] but it also yields metastable phases like y-Fe_2O_3 [38], t-ZrO_2 [39] and anatase TiO_2 [40]. The process has also been useful in preparing V^{4+} doped zircon (blue pigment) without the use of any mineralizer [41]. The advantages of the solution combustion process over other combustion methods are: firstly, being a solution process, it has control over the homogeneity and stoichiometry of the products; secondly, it is possible to incorporate desired impurity ions in the oxide hosts and prepare industrially useful materials.

The advent of the solution combustion method offers a versatile means to synthesize technologically important oxide materials. The future direction of the process will be towards the synthesis of nonoxide materials such as sulfides, nitrides, carbides and so on. There is scope, however, for further investigations to understand the mechanism of the process and the role of the fuel in controlling the particle size and the microstructure of the combustion process. Interestingly, combustion of metal nitrate-glycine–ammonium nitrate redox mixtures [41] or metal acetate–aluminium nitrate- urea mixtures exhibited non flaming linear combustion to yield nanosize oxide products [42]. Voluminous zirconia, t-ZrO_2 is formed by the combustion of aqueous solution containing a $ZrO(NO_3)_2$–glycine redox mixture. Formation of nanosize (~20 nm) t-ZrO_2 having large surface area (17 m ^{2}/g) has been confirmed by TEM and surface area measurement. Other oxides were prepared using glycine as fuels are CeO_2 –ZrO_2 and Yttria stabilized Zirconia .

Thus, Solution Combustion synthesis leads to the preparation of nanosize materials:

a. By using the precursors like metal acetates and glycine, one can control combustion and prepare nanosize oxides.
b. Carcinogenic hydrazine-based hydrazide fuels can be avoided.
c. Combustion can be initiated by microwave, which yields uniform, narrow size distribution of products.

Microwave Combustion Synthesis

Combustion process can also be initiated by irradiating metal nitrate - fuel mixtures with microwaves instead of conventional heating. This approach brings in the principles of both microwave radiation and combustion synthesis. This essentially serves as a furnace-less reaction, which makes use of microwave to initiate a self-propagating combustion reaction. Some of the compounds which have been prepared by microwave combustion are Lithium ferrites [43] used in microwave devices and memory core, YAG doped with rare earths [44] and transition compounds like Chromium [45] which is used as solid state laser material and as phosphor in variety of lamps.

Microwaves are electromagnetic radiation with wavelengths ranging from 1 mm to 1 m in free space with a frequency between 300 GHz to 300 MHz, respectively. Today microwaves at the 2.45 GHz frequency are used almost universally for industrial and scientific applications. The frequencies allotted for microwave dielectric heating (also referred to as microwave heating or dielectric heating) are 918 MHz and 2.45 GHz, with the latter frequency being used most often. The latter is also applied in domestic microwave ovens. These frequencies correspond to respective wavelengths of 33.3 and 12.2 cm which are in the region between the infrared and radiowave wavelengths in the electromagnetic spectrum.

Microwave heating is fundamentally different from conventional heating. In the microwave process, the heat is generated internally within the material instead of originating from external sources, and hence there is an inverse heating profile. The heating is very rapid as the material is heated by energy conversion rather than by energy transfer, which occurs in conventional techniques. The extent of microwave heating depends on the material being processed, and there is almost 100% conversion of electromagnetic energy into heat, largely within the sample itself, unlike with conventional heating where there are significant thermal energy losses. Microwave heating has many advantages over conventional heating methods [46, 47]; some of these advantages include, time and energy saving, very rapid heating rates (>400°C/min), considerably reduced processing time and temperature, fine microstructures and hence improved mechanical properties, it is environmentally friendly; and so on.

It is well-known that the interaction of dielectric materials with microwaves leads to what is generally described as dielectric heating [48]. Microwaves being electromagnetic waves, contain electric and magnetic field components. Electric dipoles present in such materials respond to the applied electric field of microwaves. The electric field applies a force on charged particles as a result of which the charged particles start to migrate and/or rotate. Due to the movement of charged particles further polarisation of polar particles takes place. The concerted forces applied by the electric and magnetic components of microwaves are rapidly changing in direction (2.4×10^9 per second) causing warming. The assembly of molecules, *e.g.,* a liquid or a semi-solid, cannot respond instantaneously to the changing direction of the alternating field and there results a phase lag in the reorientation and this gives rise to a polarization current which is *in phase* with the applied field. If the phase lag, field strength, and current are δ, E, and I respectively, then the component of the *in phase* current is $I \sin \delta$, (since E and I are 90° *out of phase* in an ideal dielectric). This current causes resistive heating in the medium. Thus, the reorientation dynamics of the dipoles in the applied alternating field is significant for microwave heating.

The dielectric parameters ε' and ε'' are associated with the extent of heating which the material can undergo in a dielectric field.

ε'' is the relative permittivity, which is a measure of the ability of a molecule (or assembly of molecules) to be polarised by an electric field.

ε' is the dielectric loss, which is indicative of the ability of a medium to convert dielectric energy into heat.

The exact dependence of the heating rate upon the presence of a dielectric field is given by the relation,

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

tan δ is the energy dissipation factor or dielectric loss tangent and defines the ability to convert electromagnetic energy into heat energy at a given frequency and temperature. The value of tan δ of an assembly of molecules depends on several factors like the frequency of the electromagnetic waves, the temperature, the physical state and composition of the mixture.

In materials where the dipoles rotate freely, such as in liquids, the rotational frequency of the dipole determines the dissipation of energy from the applied field. In general, the dipolar species in any medium possesses a characteristic relaxation time, τ, and the dielectric constant is, therefore, frequency-dependent.

When microwaves are incident perpendicularly on the surface of the material, its intensity decreases progressively inside the material in the direction of incidence as the microwave energy gets progressively dissipated. This is expressed through the parameter known as penetration depth, *D*, which is the distance in the direction of penetration at which the incident power is reduced to half its initial value:

$$D = \frac{3\,\lambda_0}{8.686\pi \tan \delta\, (\varepsilon')^{1/2}}$$

Here λ_0 is the wavelength of the microwave radiation. The equation suggests that there is a slight advantage in working at lower frequencies when large samples are involved, but it is compensated in terms of power absorbed per unit volume.

For most oxide materials, *D* is significantly high and, therefore, microwave power dissipation is fairly uniform throughout the material as long as the sample sizes are not large. This leads to an important feature of microwave heating, namely, volumetric heating, which results in a temperature profile exhibiting a decreasing slope toward the geometrical borders of the sample in a manner opposite to that found in conventional heating.

Dielectric properties are dependent on both the chemical composition as well as the physical state of the material e.g. impurities, aliovalent substitution and the chemical nature of the material (transition metal compound, chalcogenide etc.) can give rise to high dielectric constants and losses and result in strong microwave coupling. Similarly, powders which consist of surface defects, surface charge and polarization can also enhance the dielectric parameters which are desirable for microwave coupling. Crystal structures which support permanent polarization can similarly be expected to give rise to good microwave susceptibility. In turn it is to be anticipated that materials containing highly polarizable elements (e.g., PbS) should be good microwave susceptors. Powders of inorganic materials which are piezoelectric can give rise to resonance absorption because the thickness vibrational modes in micrometer-sized particles which lie in the microwave regime [49]. In highly ionic materials (fast ion conductors), both polarization effects associated with site to site jumps of ions and the ionic current enable them to couple well with microwaves.

In ionic materials, where ions can drift in the applied field, joule heating can occur because of the ionic current itself. Thus in such situations, the dipolar reorientation current σ_d and ion drift current, σ_i can be combined so that effectively

$$\varepsilon'' = \frac{(\sigma_d + \sigma_i)}{\omega\varepsilon_0}$$

where ε_0 is dielectric constant of free space.

In semiconducting and semimetallic materials, the conduction loss is dominated by the electronic transport. Hence $\sigma_{electronic}$, which increases with both increasing temperature and decreasing band gap, leads to high degree of microwave absorption. The microwave power dissipation per unit volume in a material, *P*, is dependent upon the total current σ and the square of the electric field *E* in the sample:

$$P = \sigma \mid E \mid^2 = (\omega \varepsilon_0 \, \varepsilon'') \mid E \mid^2$$

in terms of ε'

$$P = (\omega \varepsilon_0 \, \varepsilon' \tan \delta) \mid E \mid^2 \qquad \text{or} \qquad P = (2\pi f \varepsilon_0 \, \varepsilon' \tan \delta) \mid E \mid^2$$

The frequency, *f* and the amplitude | E | of the microwaves are instrumental parameters (controllable) while the dielectric constant ε' and the loss tangent tan δ, are material parameters and ε_0 is the permittivity of the free space. Therefore, in a given instrumental set up (with | *E* | and *f* held constant), P is determined by ε' and tan δ.

ε' is generally high for materials containing molecules or complex ions of high dipole moment and therefore, high molar polarization. Therefore, when a mixture of two materials, A and B of different dielectric constants, ε'_A and ε'_B, is exposed to microwave field, the material with higher values of ε' absorbs energy preferentially and gets heated rapidly compared to the other. For the microwave decomposition of a material in a mixture the differential absorption of microwave energy can be used to advantage. A precursor material can be chosen such that it has a high value of ε' and decomposes by preferential microwave absorption to yield the desired oxide. Thus, if a metal organic or an inorganic complex salt, of reasonably high value of dielectric constant that yields the desired oxide upon decomposition is dissolved in a suitable liquid medium of low dielectric constant and irradiated with microwaves, we can expect the formation of the metal oxide.

In microwave induced combustion synthesis, microwave irradiation couples with polar wet chemical precursors such as metal nitrate (oxidizer) and an organic fuel. The electromagnetic field polarizes these dipolar substances, which induces dipole in the molecule. As a result increased rotation sets in, which causes internal heating due to frictional effects. The microwave power P absorbed to produce internal heating is proportional to the relative dielectric constant (ε'_r) of the reaction mixture. These precursors absorb the microwave effectively involving mechanisms such as dipolar losses [50], ion jump relaxation [51] and Ohmic loss effects [52] and on decomposition yield a very fine powder, which react to form the single-phase product.

Hydrated water molecules act as a solvent enhancing the microwave power loss of the metal nitrates in two ways [53]. Firstly water has a high dielectric constant ($\varepsilon'_r = 78.4$). Secondly, it increases the polarity of the metal nitrates, allowing strong microwave coupling. Consequently

Figure 2 *Microwave Oven*

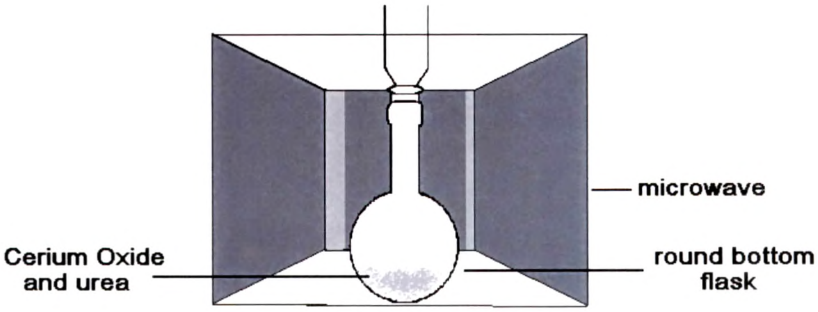

Figure 3

there is internal heating, which leads to the formation of metal oxides as a transient phase. Heat of formation of finely divided transient oxides is negative and therefore the reaction is exothermic. Hence microwave coupling and enthalpy of formation of component metal oxides contribute eventually to the thermodynamic requirements of the final phase formation. The local temperature decreases the activation energy leading to the increase in the reaction rate.

Microwave interaction of two other types can also lead to dissipation of energy very rapidly. One of them is the excitation of weak bonds such as secondary bonds in chalcogenides or interlayer bonds in graphite (and similar materials). Since microwave frequencies correspond to rotational excitation energies in materials, the incident microwaves excite the rotational modes. They are state-to-state excitations and therefore the energy absorption occurs by resonance. The absorbed energy may be completely dissipated as heat during de-excitation via internal mode coupling. The excitation of weak bonds may fall into the same general category of state-to-state excitations.

3.3 Synthesis by co-precipitation

Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes. Co-precipitation reactions tend to exhibit the following characteristics:

(i) The chemical reaction leads to supersaturating conditions necessary to induce precipitation.

(ii) The products of precipitation reactions are generally sparingly soluble species formed under conditions of high super saturation.

(iii) The conditions dictate that nucleation will be a key step of the precipitation process and that a large number of small particles will be formed.

(iv) Secondary processes, such as Ostwald ripening and aggregation, dramatically affect the size, morphology, and properties of the products.

When the product contains only one or two elements (e.g. a metal, binary oxide, etc.), precipitation reactions are relatively straightforward. In more complicated ternary and quarternary systems, the process becomes more complex, as multiple species must be precipitated simultaneously. Hence, the name *Co-precipitation* is given.

For a particular solvent, there is certain solubility for a solute, whereby addition of any excess solute will result in precipitation and formation of crystals. For nucleation to occur, the solution must be supersaturated either by directly dissolving the solute at higher temperature and then cooling to low temperatures or by adding the necessary reactants to produce a supersaturated solution during the reaction [54, 55]. The precipitation process basically consists of a nucleation step followed by particle growth stages [56, 57].

There are three kinds of nucleation processes: homogeneous nucleation, heterogeneous nucleation, and secondary nucleation. Homogeneous nucleation occurs in the absence of a solid interface by combining solute molecules to produce nuclei. It happens due to the driving force of the thermodynamics because the supersaturated solution is not stable in energy. The overall free energy change, ΔG, is the sum of the free energy due to the formation of a new volume and the free energy due to the new surface created. For spherical particles

$$\Delta G = -\frac{4}{V}\pi r^3 k_B T \ln(S) + 4\pi r^2 \gamma$$

where V is the molecular volume of the precipitated species, r is the radius of the nuclei, k_B is the Boltzmann constant, S is the saturation ratio, and γ is the surface free energy per unit surface area.

If $S > 1$, ΔG has a positive maximum at a critical size of the nuclei. This maximum free energy is the activation energy for nucleation. Nuclei larger than the critical size will further decrease their free energy for growth and form stable nuclei that grow to form particles.

After the nuclei are formed from the solution, they grow via molecular addition, which relives the supersaturated step. When the concentration drops below the critical level, nucleation stops and the particles continue to grow by molecular addition until the equilibrium concentration of the precipitated species is reached. Uniformity of the size distribution is achieved through a short nucleation period that generates all of the particles obtained at the end of the reaction followed by a self sharpening growth process. The smaller particles grow more rapidly than the larger ones because the free energy driving force is larger for smaller particles than for larger ones, if the particles are slightly larger than the critical size. Here focusing in size occurs. Monodisperse size distribution can be obtained at this stage by either stopping the reaction (nucleation and growth) quickly or by supplying reactant source to keep a saturated condition. When the reactants are depleted due to particle growth, Ostwald ripening or defocusing will occur, where the larger particles continue to grow, and the smaller ones get smaller and finally dissolve. Saturation ratio (*S*) decreases now and the corresponding critical nuclei size increases therefore any particles smaller than this new critical size will dissolve. If the reaction is quickly stopped at this stage, the particles will have a broad size distribution, which is featured by a distribution centering two size regimes, a bigger one and a smaller one, and the critical size now at this saturation is in between. Once the reaction (mainly the growth of the particles) goes into this stage, it is difficult to get monodisperse particles unless the reaction is extended to long enough times to completely deplete the supersaturation and the smaller nuclei. The size of the particles gets relatively large and can extend into the micrometer size regime.

In addition to the growth by molecular addition where soluble species deposit on the solid surface, particles can grow by aggregation with other particles, and this is called secondary growth. The rate of particle growth by aggregation is much larger than that by molecular addition. After the particles grow to a stable size, they will grow by combining with smaller unstable nuclei and not by collisions with other stable particles.

Nanoparticles are small and are not thermodynamically favoured for crystal growth kinetically. To finally produce stable nanoparticles, these nanoparticles must be arrested during the reaction either by adding surface protecting reagents, such as organic ligands or inorganic capping materials [55] or by placing them in an inert environment such as an inorganic matrix or polymers [57]. The nanocrystal dispersions are stable if the interaction between the capping groups and the solvent is favorable, providing an energetic barrier to counteract the Van der Waals and magnetic attractions between nanoparticles. To help arrest these nanoparticles, different solvents are also used to change the solubility or the reaction rate [54, 55, 57].

Many nanoparticulate metal oxides are prepared by calcining hydroxide coprecipitation products. The products of coprecipitation reactions, particularly those performed at or near room temperature are usually amorphous. In those cases where hydroxides or carbonates of mixed metals are precipitated from solution and subjected to a calcination or postannealing process, it is extremely difficult to experimentally determine whether the as-prepared precursor is a single-phase solid solution or a multiphase, nearly-homogeneous mixture of the constituent metal hydroxides-carbonates-oxides that react to form a single-phase mixed-metal oxide when heated.

The coprecipitation of metal cations as carbonates, bicarbonates, or oxalates, followed by their subsequent calcination and decomposition, is a common method for producing crystalline nanoparticulate oxides. The calcination will, however, almost invariably lead to agglomeration or, at high temperatures, aggregation and sintering. Fortunately, nanoparticulate hydroxide, carbonate, and oxalate precursors tend to decompose at relatively low temperatures (<400 °C) due to their high surface areas, thereby minimizing agglomeration and aggregation e. g. $Ce_{0.8}Y_{0.2}O_{1.9}$ was precipitated by the addition of oxalic acid to an aqueous solution of $Ce(NO_3)_3$ and $Y(NO_3)_3$, followed by calcinations [58]. Calcining at 500 °C yielded roughly spherical particles of 10 nm, which were slightly agglomerated. Calcining at 1000 °C resulted in 100 nm aggregates with irregular shapes. Lower calcination temperatures reduced aggregation considerably.

Precipitation reactions are carried out in aqueous and nonaqueous solvents. Nonaqueous solvents are used when precipitating dissimilar metals that cannot be simultaneously precipitated from aqueous solution due to large variations in the pH values necessary to induce precipitation of the constituent cations. The use of aqueous solvents is avoided specifically to prevent the premature precipitation of metal hydroxides/oxides. Premature precipitation tends to be problematic with high valence, electropositive metals such as Ti^{4+}, Zr^{4+} and so forth. This can, to some extent, be circumvented by using metal chloride/nitrate or metal alkoxide precursors in nonaqueous solvents.

Metal hydroxide gels are in general polymeric chains forming an entangled network in which solvent is entrapped. It is the osmotic pressure, which is the sum of rubber elasticity, polymer–polymer affinity and hydrogen ion pressure that contributes to stability of the gel [59]. If any one of the factors is altered, the gel collapses irreversibly. The continuous influx of solvent breaks the gel network and small crystalline regions are created. This crystallization is favoured because of reduction in the free energy. Calcining the product at a particular temperature also breaks the gel network to form small crystals.

In the present work rare earth doped metal oxide phosphors (CeO_2, La_2O_3, and ZrO_2) have been synthesized by Ceramic method (Solid State reaction), Solution Combustion Synthesis (Furnace and Microwave induced) and Co-precipitation methods.

Metal hydroxides and oxides were prepared by precipitation method in alcoholic solution, the properties of the prepared nanoparticles were studied, and the results were obtained.

Respective amounts of metal oxides were completely dissolved in conc.nitric acid (HNO_3) and evaporated to dryness to remove excess HNO_3. The metal nitrates obtained were dried by a desiccators. These nitrates were dissolved in alcohol to form 0.2mol/Lit alcoholic solution. Another solution was prepared by mixing ammonium hydroxide in alcohol forming 2mol/Lit alcoholic solution. Alcoholic solution of rare earth nitrates was added drop wise into the alcoholic solution of ammonium hydroxide which and vigorously at a temperature of 50°C.The precipitates start forming. The final pH value of the solution was greater than nine. The precipitates were filtered and washed with acetone several times to get rid of anions and ammonium ions. The precipitate was dried in vacuum desiccators for 10-12 hours and finally dried in an oven at 100°C for 12 h. The metal hydroxides nanoparticles MOH (M=Ce, Zr, La) were obtained. The rare earth oxides nanoparticles were obtained when the relevant rare earth hydroxides were calcined at different elevated temperatures. Calcination at the appropriate temperature is necessary to

(i) obtain a stoichiometric crystalline phase,
(ii) remove any residual solvent and,
(iii) obtain powders with desired agglomerate size, surface area and crystal structure according to the end applications.

This heat treatment has an important effect on the phase content, microstructure and luminescence properties of the ceramics prepared from these powders.

In Furnace combustion synthesis, metal oxides with appropriate amount of dopant were dissolved in dilute nitric acid solution in a beaker, then heated to remove the excess nitric acid. The stoichiometric compositions of these metal nitrates and fuel was calculated based on the total oxidizing and reducing valency of oxidizer and the fuel which serves as a numerical coefficient for stoichiometric balance known as equivalence ratio ϕ_e which should be unity as the energy released is maximum for this ratio. After mixing, the starting materials were placed in a Pyrex round bottom flask and mixed with deionized water. This mixture was then put in a cylindrical furnace maintained at 500°C.The furnace is shown in figure 1. After the combustion reaction resultant porous powders were crushed into finer form and heated at elevated temperatures.

Microwave-induced combustion synthesis involves the dissolution of metal nitrate and fuel in deionized water and then heating the resulting solution in a microwave oven. A domestic (LG Scientific MS283MC 850 W) microwave oven (figure 2) operating at 2.45 GHz and with a six stage variable power, modified to accommodate the round bottomed flask with the attached cylindrical column. The column was made to project out vertically from the top of the oven as shown in figure 3. The microwave power was kept at maximum so that the necessary temperature to initiate combustion process is reached faster. After the solution reaches the point of spontaneous combustion, it begins to burn in solid form burning at high temperature. The whole process takes only few minutes. The byproducts released are Carbon dioxide, water and nitrogen for both microwave and furnace combustion processes.

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