3. SYNTHESIS OF NANOSTRUCTURED MATERIALS

The present chapter deals with the different strategies developed to synthesize materials with characteristic features on the nanometer scale. We describe here briefly some of the important methods used for the preparation of nanostructured metal oxides. The microwave method is dealt within a detailed manner, more details as we have used this particular method for the synthesis of nanoparticles in the present study.

3.1 General Methods of Preparation

The preparation of nanostructured materials (NSMs) from atomic or molecular sources depends on the control of variety of nanoscale attributes desired in the final product. In general, the following four methods have been used to make nanophase materials [1].

1. The first technique involves the production of isolated, ultrafine crystallites having uncontaminated free surfaces followed by a consolidation process either at room temperature or at elevated temperatures. The specific processes used to isolate the NSMs are, for example, inert-gas condensation, decomposition of the starting chemicals or the precursors, and precipitation from solutions.

2. Chemical vapour deposition (CVD), physical vapour deposition (PVD), and some electrochemical methods have been used to deposit atoms or molecules of materials on suitable substrates. Nanocomposites can be produced by depositing chemically different molecules simultaneously or consecutively.
3. By introducing defects in a formerly perfect crystal such as dislocations or grain boundaries, new classes of NSMs can be synthesized. Such deformations may be brought about by subjecting the materials to high energy by either ball milling, extrusion, shear, or high energy irradiation.

4. The final approach used to make NSMs is based on crystallization or precipitation from unstable states of condensed matter such as crystallization from glasses or precipitation from supersaturated solid or liquid solutions.

Although these are the general methodologies employed in the preparation of nanostructured materials, several variants of these processes have been developed to generate compounds or alloys with specific composition and properties and also for optimized production.

The first commonly accepted systematic classification of synthetic routes focuses on the general strategy applied by the synthetic method and identifies two major categories, usually termed “top-down” and “bottom-up” [2-6]. The conceptual framework is schematically described in Figure 3.1.

![Figure 3.1](image_url): Schematic representation of “bottom-up” and “top-down” approaches for the synthesis of nanometer-sized materials
The “top-down” strategy relies upon the synthesis of nanometer-sized systems by the progressive fragmentation of a massive crystal. This generally results in an increase of the number of coherent crystalline domains accompanied by a decrease of their average size. Therefore, the experimental “top-down” processes typically generate a nanostructured phase characterized by individual nanometer-sized coherent crystalline domains separated by thin structurally disordered boundaries.

In contrast, the “bottom-up” approach is based on the gradual assembly of small building blocks consisting of either individual atoms and molecules or suitable nanometer-sized systems. Accordingly, individual nanomaterials are prepared starting from precursors or reactants at the atomic or molecular level. Depending on the fundamental mechanisms, these methods allow the fabrication of systems with various architectures such as particles, wires and tubes. It follows that, at least in general terms, the “bottom-up” approach exhibits the highest synthetic versatility. The two above mentioned strategies find application in a number of experimental techniques exploiting the physical, chemical or physico-chemical processing of gaseous, liquid and solid phases as well as of their possible different mixtures.

3.2 Precipitation Method

In this method solution chemistry is used to prepare the precursor, which is subsequently converted to the nanophase particles by nonliquid phase chemical reactions. Precipitation of solid from a solution is a common technique for the synthesis of fine particles. Many ionic reactions in aqueous solution result in the formation of a solid phase. When precipitation and dissolution reactions are
reasonably rapid, equilibrium calculations can be applied to describe the process.

A typical precipitation reaction is represented by:

\[ A + B \leftrightarrow AB \; (\text{solution}) \leftrightarrow AB \; (\text{solid}) \]

where AB(solid) denotes AB in the solid phase.

In order that a precipitate shall form, it is not sufficient merely to exceed the equilibrium solubility, an appreciably greater concentration, the super saturation limit, must be exceeded. Thus, although solutions containing solute in excess of its solubility are thermodynamically unstable, that is, they are metastable, and they do not give rise to a precipitate until this super saturation concentration exceeds the super saturation limit and the solution becomes 'labile'.

Precipitation can be considered as a two - stage process, the formation of nuclei, followed by their growth into the precipitate particles that are eventually obtained.

3.2.1 Nucleation

Nuclei are the smallest particles of precipitate capable of spontaneous growth in a medium supersaturated with solute. The formation of these particles is termed nucleation and this must take place before precipitation can occur.

In the simplest examples of nucleation, atoms/ions/molecules are assumed to form clusters of increasing size by a series of reversible reactions:

\[ A + A \leftrightarrow A_2 \]
\[ A_2 + A \leftrightarrow A_3 \]

..............................

..............................

\[ A_{n-1} + A \leftrightarrow A_n \; (\text{cluster}) \]
Addition of further atoms/ions/molecules to the critical cluster would result in nucleation and subsequent growth of the nucleus. The construction process, which occurs very rapidly can only continue in local regions of very high supersaturation, and many of the embryos or “sub-nuclei” fail to achieve maturity; they simply redissolve because they are extremely unstable. If, however, the nucleus grows beyond a certain critical size it becomes stable under the average conditions of supersaturation obtaining in the bulk of the fluid.

The time that elapses between the mixing of reactants and the appearance of a precipitate is called the induction period.

Nucleation can be facilitated by the introduction of suitable submicroscopic particles into the solution. A commonly used procedure is to produce minute glass fragments by scratching the walls of the precipitation vessel. A similar effect is achieved by adding traces of certain sparingly soluble species.

3.2.2 Crystal Growth

The subsequent spontaneous growth of the nuclei to form the final particles of precipitate soon overtakes nucleation as the predominant process in the reaction. It continues until the solubility product is no longer exceeded. In general, the rate of growth of the particles increases with increasing super saturation, but an increased growth rate also gives rise to an increased number of imperfections in the resulting crystals. Thus, very large super saturation results in the rapid precipitation of imperfect and extremely small particles, so that an amorphous, gelatinous precipitate is produced.
It has been employed to prepare ceramic composites containing metal carbides. One disadvantage of this method resides in the difficulty in controlling the particle size and size distribution. Fast precipitation often takes place, resulting in large particles [7].

3.3 Microemulsion Method

A microemulsion can be defined as the thermodynamically stable, optically clear dispersion of two immiscible liquids (water and oil) consisting of nano-sized domain of one or both liquids, that are stabilized by an interfacial film of surfactants molecule.

Microemulsions are generally classified into two types – oil in water (O/W) and water in oil (W/O). In O/W type microemulsions, the bulk phase is water and these are called normal micelles. In W/O type of microemulsion, the bulk phase is oil and these are known as reverse micelles. The water in oil microemulsion (W/O), or reverse micelles consist of nano-sized water droplets which are dispersed in the continuous hydrocarbon phase and stabilized by surfactant molecules accumulated at the O/W interface. The surfactant most often used is sodium 2-bis(2-ethylhexyl) sulfosuccinide, Na(AOT). The thermodynamically stable dispersion, microemulsion can be used to carry out chemical reactions, and particularly synthesize different nanomaterials with new and special properties. It can be used as nano reactors to produce nanoparticles by carrying out chemical reactions in their aqueous core and also prevents aggregation of particles by acting like cage. Solvent removal and subsequent calcinations lead to the final product. This technique does not require any special equipment and extreme conditions of temperature and pressure for
processing. It is possible to control the size and morphology of particles formed
disadvantages include low production yields and complex operations.

3.4 Thermal Decomposition

Thermal decomposition is usually carried out using complex element-organic
and organometallic compounds, hydroxides, carbonyls, formates, nitrates, oxalates,
amides and imides of metals which at a specific temperature decompose with the
formation of a synthesized substance and generation of the gas phase.

Principally the ratios of the starting reagents including organometallic
compounds, surfactants, and solvents are the decisive parameters for controlling the
size and morphology of magnetic nanoparticles (MNPs). The reaction temperature
and time, as well as the aging period may also be crucial for the precise control of
size and morphology [8].

Up to date, two different approaches have been used for this purpose.
First, thermal decomposition of metal carbonyl precursors followed by an oxidation
step using air [9], or oxidation by using an oxidant at elevated temperatures [10].
The second is decomposition of precursors with a cationic metal center in the
absence of reducing agents [11]. The presence of reducing agents leads to metal
nanoparticles even by the use of cationic precursors [12].

Thermal decomposition seems the best method developed for size and
morphology control of NPs. Also, the yield of production is high and scalable.
However, one of the major disadvantages of this method is the production of organic
soluble NPs which limits the extent of application uses of them in biological fields
besides surface treatment is needed after synthesis; also, thermal decomposition
methods usually lead to complicated processes or require relatively high temperatures. And other one disadvantage is the relatively low selectivity of the process, because the reaction product is usually a mixture of the target product and other compounds.

3.5 Hydrothermal Synthesis

In this method/synthesis, the reactions are performed in aqueous media in reactors or autoclaves where the pressure can be higher than 2000 psi and the temperature can be above 200 °C. Hydrothermal methods rely on the ability of water to hydrolyze and dehydrate metal salts on elevated conditions, and the very low solubility of the resulting metal oxides in water at these conditions to generate supersaturation [13]. Hao and Teja [14] conducted a detailed investigation of the effects of precursor concentration, temperature, and residence time on particle size and morphology in this method. The particle size and size distribution increased with precursor concentration. However, the residence time had a more significant impact on the average particle size than feed concentration. Monodispersed particles were produced at short residence times. Xu and Teja [15] have also employed the continuous hydrothermal method to produce polyvinyl alcohol (PVA) coated iron oxide nanoparticles. PVA was chosen as the coating material because it has the desired solution properties in water and it contains many isolated hydroxyl functional groups, which can absorb and complex with metal ions. The results of their experiment showed that particles with uniform shape and narrow particle size distribution were obtained in the presence of PVA. The average particle size decreased with increasing PVA concentration when the residence time was of the order of 2 s, and became nearly independent of PVA concentration when the
residence time was 10 s or higher [16]. Particle size and morphology control is one of the advantages of hydrothermal techniques. It is also easy to scale up. But additional post-processing steps are required, to achieve the engineering of particle surfaces.

### 3.6 Solvothermal Method

The main difference between hydrothermal and solvothermal methods for the synthesis is the substitution of some or all of the water with another solvent. The choice of solvent depends on the goal of the experiment. In the case of the formation of ferrites, the properties of the solvent are manipulated by adding alcohols such as ethanol or isopropanol to water [17]. The alcohol influences the reaction path by providing a reducing environment. By changing the solvent composition, the reaction as well as the solvent properties can be manipulated. Once again, however, particle size is typically closer to a micron. While there are other supercritical solvents that can be used, the formation of oxides requires a source of oxygen or hydroxide anions. Therefore, water and alcohols are best suited for this case. The trends of solvothermal synthesis are similar to those observed in hydrothermal processing.

### 3.7 Sol-gel Method

Sol-gel technology is a good example of an apparently simple technology, but one with a great variety of scientific possibilities and industrial applications. The process is typically used to prepare metal oxides and the hydrolysis of reactive metal precursors, usually in a solution, resulting in the corresponding hydroxide. Condensation of the hydroxide molecules by elimination of water leads to the
formation of a network of metal hydroxide. When all hydroxide species are linked in one network like structure, gelation is achieved and a dense surrounding interconnected pores. Removal of the solvents and appropriate drying of the gel results in a ultrafine powder of the metal hydroxide. Further heat treatment of the hydroxide leads to the corresponding ultrafine powder of the metal oxide. The innovation of the sol-gel process in forming powders is that the powder size, morphology, and surface chemistry are controlled simultaneously. It is implement of great interest all along for several reasons: a) it seems to have almost unlimited potential in terms of the variety of materials and products that can be produced; b) it promises to be an inexpensive method for producing a large number of nanomaterials; c) it is the only method to make intimate, homogeneous mixtures of nanoparticles in the liquid phase; d) it is the only general method to produce inorganic-organic polymers and other mixtures; e) it holds strong promise for implement on large scales [7].

Sol-gel processes can be used to prepare a variety of materials including glass, powders, films, fibers, and monoliths [18,19]. Traditionally, sol-gel process involves hydrolysis and condensation of metal alkoxides. Factors that need to be considered in a sol-gel process are solvent, temperature, precursors, catalysts, pH, additives, and mechanical agitation. These factors can influence the kinetics, growth reactions, hydrolysis, and condensation reactions. The solvent influences the kinetics and conformation of precursors, and the pH affects the hydrolysis and condensation reactions, and also the isoelectric point and the stability of the sol. These factors finally decide the aggregation and particle size. By varying the factors that influence the reaction rates of hydrolysis and condensation, the structure and
properties of the gel can be tailored. So far, sol-gel process has been used to prepare pure, stoichiometric, dense, equiaxed, and monodispersed particles. It should be noted that sol-gel method is particularly attractive for the synthesis of multicomponent particles with binary or ternary compositions using double alkoxides, or mixed alkoxides. Hybrid materials such as metal-oxide, organics-oxide can be prepared using the sol-gel approach.

3.8 Template Synthesis

Mesoporous materials and anodized aluminum oxide (AAO) with uniform pore sizes can be good templates for synthesizing nanoparticles. These templates can also be considered to be nanoreactors, in which chemical reactions take place. Their confined pore sizes will guide the NPs and can deliver a controllable size distribution to the final product. For instance, the mesoporous materials can shape the NPs in sizes ranging from 2 to 50 nm. Generally, the introduction of semiconductors into mesoporous materials can produce regular NPs with well-controlled particle sizes and distributions.

Two methods are used to load semiconductor NPs into pores of a mesoporous material: in situ or post-treatment. The former method is accomplished by mixing the NPs precursors with the micelles before the formation of the mesopores; the latter by directly grafting the NPs onto the pore surfaces of an as-prepared mesoporous material. Multiple means of post-treatment have been successfully explored, including surface grafting via sorption, phase transitions, ion exchange, complexation, and covalent grafting.
3.9 Electrochemical Synthesis

Reetz and others [20-28] have pioneered the electrochemical synthesis of metal nanocrystals. Their method represents a refinement of the classical electro-refining process and consists of six elementary steps. They are oxidative dissolution of anode, migration of metal ions to the cathodes, reduction of ions to zero-valent state, formation of particles by nucleation and growth, arrest of growth by capping agents, and precipitation of particles. The capping agents are typically quaternary ammonium salts containing long-chain alkanes such as tetraoctylammonium bromide. The size of the nanocrystals could be tuned by altering the current density, the distance between the electrodes, the reaction time, the temperature, and the polarity of the solvent.

3.10 Aerosol/Vapour-Phase Method

This method involves the vapourization onto a substrate of an organic solution containing ferric salts and a reducing agent (also known as spray pyrolysis) [29-32]. The resulting fine droplets are transformed into NPs (whose size depends on the droplet size), following the evaporation of the organic solvent. Alternatively, a laser may be used to heat a gaseous mixture of iron precursor (e.g., iron pentacarbonyl). This route is also known as laser pyrolysis. The reaction is performed continuously into generators in order to reach high yields.

3.11 Chemical Reduction

This method is also a solution-phase chemistry route developed for the preparation of metal NPs. Here, the reduction of metal salts is the most common, and reducing agents such as NaBH₄ [33-36] have been commonly employed in the
reactions. A key advantage of this method is its simplicity. It can be safely done in most chemistry labs with simple chemical reagents. Also, this reaction can be done at room temperature conditions.

3.12 Sonochemical Method

The sonochemical method is a competitive alternative to other time-consuming preparation techniques. It has been extensively used to generate novel materials with unusual properties. The physiochemical effects of ultrasound arise from acoustic cavitation, which comes from the formation, growth and implosive collapsing of bubbles in the liquid. The implosive collapsing of the bubbles generate a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hotspots have been experimentally determined, with transient temperatures of 5000 K, pressures of 1800 atm and cooling rates beyond $10^{10}$ Ks$^{-1}$. These extreme conditions were beneficial to forming the new phase and have a shear effect for agglomeration, which is necessary to prepare the high monodispersive nanoparticles [37].

3.13 Combustion Method

Combustion synthesis is a promising solution-chemistry route for synthesizing a variety of oxide ceramics in the nano crystalline form. The combustion technique is capable of producing the nano crystalline powders of oxide ceramics at a lower calcination temperature in a very short time [38-40]. The combustion technique involves an exothermic decomposition of a fuel oxidant precursor and results in either the powder with the required phase or a semi-
decomposed precursor with carbonaceous residue depending on the nature of the fuel and its amount used in the process. The formation of a viscous gel is a primary condition for the homogeneity among constituents and thereby preventing the selective precipitation or phase separation. The very high exothermicity generated during combustion manifests in the form of either flame or fire and hence, the process is termed as auto-ignition process. Generally, the powder obtained by this technique has the highest degree of phase purity coupled with the improved powder characteristics like narrow particle size distribution, higher surface area and better sinterability.

3.14 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a well known process in which a solid is deposited on a heated surface via a chemical reaction from the vapour or gas phase. A schematic diagram is shown in Figure 3.2.

![Schematic diagram of the CVD process](image)

**Figure 3.2** : Schematic diagram of the CVD process
In the chemical vapour deposition process, a carrier gas stream with precursors are delivered continuously by a gas delivery system to a reaction chamber maintained under a vacuum at high temperature (> 900 °C) [13,41]. The CVD reactions take place in the heated reaction chamber and the products combine to form clusters of NPs. Growth and agglomeration of the particles are mitigated via the rapid expansion of the two phase gas stream at the outlet of the reaction chamber. The subsequent heat treatment of the synthesized nanopowders in the various high-purity gas streams allows compositional and structural modifications including particle purification and crystallization as well as transformation into a desirable size, composition, and morphology [13,42]. The success of this method depends on the low concentrations of the precursor in the carrier gas as well as rapid expansion and then the quenching of the nucleated clusters or nanoparticles as they exit from the reactor [13].

3.15 Arc Discharge

The principle of this technique is to vapourise carbon in the presence of catalysts (iron, nickel, cobalt, yttrium, boron, gadolinium, and so forth) under reduced atmosphere of inert gas (argon or helium). After the triggering of the arc between two electrodes, a plasma is formed consisting of the mixture of carbon vapour, the rare gas (helium or argon), and the vapours of catalysts. The vapourisation is the consequence of the energy transfer from the arc to the anode made of graphite doped with catalysts. The anode erosion rate is more or less important depending on the power of the arc and also on the other experimental conditions. It is noteworthy that a high anode erosion does not necessarily lead to a high carbon nanotube production.
Figure 3.3 shows the schematic diagram of arc discharge method. It consists of a cylinder of about 30 cm in diameter and about 1m in height, equipped with diametrically opposed sapphire windows located so that they face the plasma zone in view of observing the arc. The reactor possesses two valves, one for carrying out the primary evacuation (0.1Pa) of the chamber and the other permitting it to fill with a rare gas up to the desired working pressure.

In the arc discharge method, a DC bias of 20–30 V is applied between two carbon electrodes in a helium atmosphere. Carbon atoms are ejected from the anode, and accumulate in the form of nanotubes on the cathode. The electrodes are typically 5–20 mm in diameter. As with laser evaporation, the anode includes small quantities of nickel, cobalt or iron, which are also deposited onto the cathode to act as a catalyst. Arc discharges tend to produce narrower and shorter tubes than those obtained from laser ablation (up to 5 nm in diameter and around 1mm long). Like laser ablation method, arc discharges tend to produce bundles of nanotubes.

### 3.16 Laser Pyrolysis

It is a gas-phase process in which light at 10.6 μm from a continuous-wave carbon dioxide (CO$_2$) laser is absorbed by a material in a flowing gas stream; the absorbed energy is then transferred to non-laser active molecules in the steam. The end product, is a range of nanoscale particles with great relevance to photonics. The resulting materials can be used as phosphors for solid-state lighting, high-refractive-index fillers for optical polymer composites, thermochromic materials, and doped-glass films for planar photonics. Schematic view of the laser pyrolysis apparatus is shown in Figure 3.4.
Figure 3.3: Schematic diagram of arc discharge method

Figure 3.4: Schematic representation of the laser pyrolysis apparatus. 
[(1) Laser beam; (2) precursor; (3) reaction chamber; (4) metal filter]
There is more than one way to carry out laser pyrolysis (which can include photosynthesis, or light-initiated molecular dissociation, as well). First, precursor materials can react or decompose to form nanoparticles. Second, sensitizers can cause other materials to decompose. Finally, substances can decompose by triggering the decomposition of other substances [43]. In any case, the reactants are subsequently quenched at a controlled time to form nanoparticles, and then the particles are collected.

3.17 Microwave Method

Microwave heating has been known since the early 1940s, and has been used successfully in the food industry. Microwave chemistry has received great attention in recent years, as its use has been started in preparative chemistry and material synthesis since 1986 [44,45]. The greatest advantage of microwave irradiation is that it can heat a substance uniformly through a glass or plastic reaction container, leading to a more homogeneous nucleation and a shorter crystallization time compared with those for conventional heating.

This method provides promising alternatives for the processing of chemicals, ceramics, composites and minerals both in bulk and powder form. The technological potential of Microwave Processing (MWP) directly originates from the properties of microwaves. First employed during the World War II in radar applications, microwaves are electromagnetic waves in the wavelength domain between 300 MHz and 300 GHz. Industrial microwave processing is usually accomplished at the frequencies specifically set aside for industrial utilization, namely 915 MHz, 2.45 GHz, 5.8 GHz and 24.124 GHz [46,47]. However,
microwave furnaces with variable frequencies, usually in the range between 0.9 and 18 MHz, have also been developed for fundamental research applications [48].

Microwave processing (heating) method is carried out inside so-called furnaces which consist of a microwave radiation source, a waveguide, an applicator to deliver the power to the sample, and a system to control heating [40-42]. A schematic description of a typical furnace for MWP is shown in Figure 3.5. The choice of the applicator to employ to perform MWP depends on the properties of the material to be processed.

The absorption of the microwave electromagnetic field is directly connected with the dielectric properties of the material [40-42]. The interaction of microwaves with the material at a molecular level induces the translational and vibrational motion of both free and bound electric charges as well as the rotational motion of dipolar structures. The distribution of kinetic energy on the different translational, rotational and vibrational modes determines a general excitation of the solid, which induces a response mediated by inertial, elastic and local frictional forces. The result is a temperature rise uniformly distributed inside the sample volume. The heating rate, *i.e.* the rate at which temperature increases, depends on the strength of interaction between the material and the electromagnetic field. The electromagnetic power absorbed by the material exhibits a linear dependence on the frequency of the microwave, on the relative dielectric constant, on the so-called loss tangent that measures microwave absorptivity, and on the square of the electric field amplitude. The penetration depth, *i.e.* the distance at which the power of the incident electromagnetic waves is reduced by one half, is also dependent on such factor. More specifically, it changes linearly with the electromagnetic radiation wavelength. The limitation is that insulating systems with low dielectric loss factors are difficult to get heated as a consequence of the limited absorption of microwaves.
3.17.1 Mechanism of microwave heating

Microwaves are a form of electromagnetic energy. The frequency of microwaves ranges from 300 to about 300,000 megahertz (MHz). For microwave heating, 2450 MHz is preferred in the laboratory because it has the right penetration depth to interact with laboratory scale samples [49].

Microwave energy consists of an electric field and a magnetic field. During microwave irradiation, only the electric field transfers energy to heat a substance. The microwave photon energy (0.037 kcal/mole) is very low compared with the typical energy required to cleave molecular bonds (80-120 kcal/mole). Therefore, microwaves will only affect the molecular rotation but not the structure of the molecule.

Figure 3.6 shows the scheme of solution heating by conventional and microwave methods. For conventional heating, temperature is obtained through conductive heating with an external heat source. Thus, conventional heating results in a higher external temperature than the internal temperature. It takes time to achieve thermal equilibrium between the outside and inside of the solution. Therefore, conventional heating is inefficient and time-consuming. Microwaves heat reaction solutions through a different way. Microwaves couple directly with the molecules in the reaction solution through dipole rotation or ionic conduction. Dipole rotation and ionic conduction are two fundamental mechanisms for energy transfer from microwaves to the solution being heated.

Dipole rotation is an interaction in which polar molecules align themselves with the changing electric field of the microwaves. The rotational motion of the molecule leads to energy transfer. The coupling ability of dipole rotation is dependent on the polarity of the molecules. The higher the polarity of the molecule, the greater is its ability to couple with the microwave energy. Ionic conduction is due to free ions or
**Figure 3.5:** A typical furnace employed to submit materials to MWP

**Figure 3.6:** Schemes of conventional and microwave heating
Ionic species in the reaction solution being heated through ionic conduction mechanism, the electric field leads to ionic motion as the molecules orient themselves to the changing electric field of the microwaves. By these two mechanisms, microwaves transfer energy in $10^{-9}$ seconds (with a frequency of $10^9$ Hz) with each cycle of electromagnetic energy. The kinetic molecular relaxation from this energy is approximately $10^{-5}$ seconds. Therefore, the energy transfers faster than the molecules can relax, resulting in the non-equilibrium condition and high instantaneous temperatures. Through microwave heating, reaction rate can also be increased.

Arrhenius reaction rate equation is given as follows:

$$k = Ae^{-E_a/RT},$$

where $k$ is the reaction rate coefficient, $A$ is a constant (affected by the collision frequency between molecules and by the fraction of those molecules that have the minimum energy required to overcome the barrier of the activation energy), $E_a$ is the activation energy (energy difference between energy level of reactants and a higher transition state energy level), $R$ is the universal gas constant ($R = 8.314 \times 10^{-3}$ kJ mole$^{-1}$K$^{-1}$), and $T$ is the absolute temperature.

Microwave irradiation does not affect the activation energy. Due to the high instantaneous heating by microwave irradiation, energetic collisions are generated much faster than by conventional heating. Therefore, reaction rates can be increased. The efficiency of microwave heating depends on the solvents of the reactions.

3.17.2 Selection of solvents used in microwave-assisted techniques

With microwave heating, solvents play an important role in solution reactions. The more efficiently a solvent couples with the microwave energy the faster the
increase in temperature of the reaction solution. The polarity of a solvent plays a significant role. The higher the polarity value of the solvent the greater is its ability to couple with the microwave energy.

Many factors affect the polarity of a solvent such as the dielectric constant ($\varepsilon'$) and dielectric loss factor ($\tan \delta$). These constants contribute to the solvent’s absorbing ability. The dielectric constant is the ratio of the electrical capacity of a capacitor filled with the solvent to the electrical capacity of the evacuated capacitor ($\varepsilon' = C_{\text{filled}}/C_{\text{evacuated}}$). The product of $\varepsilon'$ and $\tan \delta$ is represented as $\varepsilon''$.

**Table 3.1:** Dielectric constants ($\varepsilon'$), and dielectric loss factors ($\tan \delta$) for some common solvents (measured at room temperature and 2450 MHz)

<table>
<thead>
<tr>
<th>Solvent (b.p. in °C)</th>
<th>$\varepsilon'$</th>
<th>$\tan \delta$</th>
<th>$\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol (197)</td>
<td>37.0</td>
<td>1.350</td>
<td>49.950</td>
</tr>
<tr>
<td>Dimethylsulfoxide (189)</td>
<td>45.0</td>
<td>0.825</td>
<td>37.125</td>
</tr>
<tr>
<td>Water (100)</td>
<td>80.4</td>
<td>0.123</td>
<td>9.889</td>
</tr>
<tr>
<td>Ethanol (78)</td>
<td>24.3</td>
<td>0.941</td>
<td>22.866</td>
</tr>
<tr>
<td>Methanol (65)</td>
<td>32.6</td>
<td>0.659</td>
<td>21.483</td>
</tr>
<tr>
<td>Acetone (56)</td>
<td>20.7</td>
<td>0.054</td>
<td>1.118</td>
</tr>
</tbody>
</table>

The dielectric parameters ($\varepsilon'$, $\tan \delta$ and $\varepsilon''$) are related to the ability of a solvent to absorb microwave energy. The dielectric loss factor is the most indicative factor. The higher the dielectric loss value of the solvent, the more efficiently the solvent converts microwave energy into thermal energy, and the faster the temperature of the solvent can be increased. Table 3.1 presents values of $\varepsilon'$, $\tan \delta$ and $\varepsilon''$ for some common solvents, measured at room temperature and at a frequency of 2450 MHz.
According to the $\varepsilon''$, the common solvents can be categorized as high, medium and low absorbing solvents. High absorbing solvents have $\varepsilon''$ values ranging from 14 to 50. Medium absorbers generally have $\varepsilon''$ values between 1.00 and 13.99. The low absorbing molecules have $\varepsilon''$ values less than 1.00. High and medium absorbers are normally used as solvents in microwave-assisted reaction due to their efficient and fast heating. Low absorbers (nonpolar solvents) are not normally used in microwave-assisted reactions.

Based on this, ethylene glycol, methanol, and ethanol (which are all high absorbers) are good solvents for chemical reactions under microwave irradiation. In the present research work, ethylene glycol was chosen as the solvent.

### 3.17.3 Novelty of microwave-solvothermal method

Microwave-assisted solvothermal synthesis is a much faster process, simpler and more efficient in energy consuming. This has got many novelties over other methods which are complicated by the long duration and elevated temperature. Unlike conventional methods, where heat is transferred from the outside to the inside, in this method, heat is generated from the interior of the material and the developed heat reduces the reaction time, energy, cost and enables the synthesis with a high yield.

Compared with the other conventional methods, the most obvious advantages of microwave-assisted solvothermal method are:

(i) The reactions are conducted at normal atmospheric pressure and at the boiling temperature of the solvent;

(ii) The simple exothermic nature of this reaction avoids the need for expensive processing facilities and equipment;

(iii) The short reaction time results in low operating and processing costs;
(iv) Usually the products show a very low level of impurities;

(v) Very simple reagents can be used as precursors; and

(vi) There are excellent reproducibility and high yields of products.

These advantages make microwave-assisted solvothermal synthesis applicable as an efficient and economical technique for the production of inorganic nanomaterials.

References


