CHAPTER - 2

Experimental Methods

2.1 Nanoscience and Nanotechnology

In last decade, new vision in material science widely defined as ‘nano science and nanotechnology’ has globally emerged. Nanotechnology is the manipulation of material on an atomic, molecular and supramolecular scale. Earlier, widespread description of nanotechnology referred to the particular technological goal of precisely manipulating atoms and molecules for fabrication of macro scale products, also known as molecular nanotechnology [1-3]. The prefix nano in the words nanoscience and nanotechnology comes from Greek word nanos meaning “dwarf” [1]. It means one part of a billion, 1 x 10^{-9} [1-3].

Nano science is basically study of size of particles within the range of 1 to 100 nm at least in one of the three dimensions. On the other hand, Nanotechnology means any technology performed on a nanoscale that has applications in the real world [4]. Nanotechnology involves the construction and application of optical, mechanical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions. Nanotechnology is likely to have a reflective impact on our daily life and humanity in the early twenty-first century, comparable to that of semiconductor technology, information technology, wireless technology and molecular biology [5-8].

The Royal Academy of Engineering, UK describes nanoscience as “the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale"[9]. Strong shells of an abalone, a mollusk, which contain nanomaterials of calcium carbonate, are a natural example.

Directly or indirectly people have been encountering the result of nanomaterials from earlier time. Lycurgus Cup, a 4^{th} century Roman cup which changes color from green to deep red when a light source is placed inside it, is found to contain silver and gold nanoparticles [2,10]. Beautiful colors of window glasses of the medieval cathedrals are due to presence of metal nanoparticles. In 1857, Michael Faraday tried to clarify effect of metal particles on the color of the church windows [3].

Current development in the field of nanoscience and nanotechnology stem from the classic lecture "There's Plenty of Room at the Bottom" given by Richard Feynman in 1959 at Caltech. In his lecture, he discussed possibility of manipulating materials at atomic scale. He imagines the whole volumes of the Britannica Encyclopedia written in a pin head [3, 11, 12]. Eric Drexler et al., in their well coveted book, Unbounding the Future, imagine a vast industrial revolution of the unprecedented size and scale [13]. Since then lot of research is carried out throughout the world on nanoscience and nanotechnology with the purpose of evaluating its potentials for scientific and technological advancement. As a result new types of materials which possess physical and chemical properties which are not observed in bulk counterpart were discovered [14-17]. In 1985, Harold Kroto and co-workers discovered a new allotrope of carbon, fullerene (C_{60}) [15]. In 1990s, Iijima discovered another allotrope of carbon, called carbon nanotubes, and phenomena of superconductivity and ferromagnetism were found in C_{60} [3, 16]. In 2004, a graphitic films called graphene was discovered by Novoselov *et al* [14]. Now, the field garnered increased scientific, and commercial attention that directed to both controversy and progress throughout the World [2,3]. Meanwhile, commercialization of products based on nanotechnology increases day by day. In future, nanotechnologies hope to provide solutions to all kind of mankind's problems whether it be hunger in the developing countries and pollutions in the developed ones [13].

Nanoscience and nanotechnology deal with materials, called nanomaterials, having size scales within 1 to 100 nm, at least in one dimension [2,3,18]. Literally, 1 nm is the length of ten H-atoms (Bohr radius = 0.5 Å) [2]. The nanoparticles can be broadly divided according to their dimensions, i.e. the degree of restriction of charge carriers (a) 1-dimension (1D), e.g. thin films whose thickness is less than 100 nm, (b) 2-dimensions (2D), e.g. Nanowires and (c) 3-dimensions (3D) i.e. confined in all three dimensions, e.g. quantum dot. Because of this reduced size (> 100 nm) with any required degree of confinement leads to increase in proportion of atoms in the surface and near surface layers thus quantum size effect[4,7,19-39]. In this size regime the properties such as melting point, colour (i.e. bandgap and wavelength of optical transitions), ionisation potential, hardness, catalytic activity and selectivity,[4,40-54] or magnetic properties such as coercivity, permeability and saturation magnetisation, which we are used to thinking of as constant, vary with size and shape.

The nanomaterial channels between atoms and molecules to macroscopic and bulk materials (> 100 nm). It exhibits new properties, different from their bulk counterparts, which depend on the material size [2,3, 55]. As such, the electronic structure, conductivity, melting temperature, mechanical properties, etc. has been reformed when material sizes are smaller than a critical size. For example, malleability and ductility of bulk copper are lost when the size is reduced to 50 nm and it becomes super hard material that do not exhibit the same malleability and ductility as bulk copper; gold nanoparticles appear deep red to black in solution as different from ordinary yellowish gold, etc. Size dependent properties allow one to change the properties of nanomaterials. This is the key to attraction in nanomaterials research. Indeed, surface to volume ratio of nanomaterials increases as the size decreases which makes possible new quantum mechanical effects and hence its properties change as the size changes in nano regime [2,3,17,18,55]. Current interesting research areas which are incorporated by nanoscience and nanotechnology, research on luminescence(optical) properties of nanomaterials is one among them. The optical bandgap and photoluminescence emission of binary II-VI semiconductors can be modified in the entire visible range of light spectrum with the variation of size. [4, 28, 56-66] Due to this variation in novel physical and chemical properties of nanoparticles with size will lead to unique applications. Production of different colors from the same material by tuning the size of a semiconducting nanomaterial is well established. For example, Cadmium Selenide (CdSe) can be tuned to emit different color by tuning size of the nanomaterial [55, 17,18].

Nanoscale materials often exhibit property which is intermediate between individual atom/molecule and bulk solid. Such behaviour of particles in the nanoscale range can be broadly divided into two types (a) Scale effects: Surface atoms are different from bulk atoms. As the particle size increases, the surface to volume ratio decreases equivalently to the inverse particle size [4]. Thus, all properties which depend on the surface to volume ratio change continuously and extrapolate gradually to bulk values and (b) Quantum effects: When the molecular electronic wave function is delocalised over the entire particle then a small, molecule-like cluster has discrete energy levels so that it may be regarded like an atom (sometimes called a super atom) [4]. The quantum effect is more pronounced with small particle system. The quantum size effect of nanoparticles can only be explained with the laws of quantum mechanics [7].

2.2 Hydrothermal Synthesis

2.2.1 Introduction

The hydrothermal synthesis is a non-conversional method to obtain nano size crystal. The hydrothermal technique is becoming one of the most significant tools for advanced materials production. Nano materials have been used in variety of technological applications such as electronics, optoelectronics, ceramics, magnetic data storage, biomedical, catalysis, biophotonics, etc. It also offers a unique method for coating of various compounds on metals, polymers and ceramics as well as for the fabrication of powders or bulk ceramic bodies. The hydrothermal technique not only helps in processing mono dispersed and highly homogeneous nanoparticles, but also acts as one of the most attractive techniques for processing shaped nano crystal and nano composite materials. This synthesis method uses the solubility in water of almost all inorganic substances at elevated temperature and pressures, and subsequent crystallization of the dissolved material from the fluid. Water at elevated temperatures plays an essential role in the precursor material transformation. The pressure, temperature, precursor concentration and time of reaction are the principal parameters in hydrothermal processing. It has emerged as a frontline technology for the processing of advanced materials for nanotechnology from last decade

2.2.2 History

The Hydrothermal Technique has been the most widespread one, garnering attention from scientists and technologists of different disciplines, particularly in the last fifteen years. The word "*hydrothermal"* has geological origin. An understandable word, "hydro" means water and "thermal" means heat. British Geologist, Sir Roderick Murchison (1792–1871) was the first to use this word. He described the action of water at eminent temperature and pressure. At these conditions, the earth's crust leading to the formation of various rocks and minerals [67]. The first publication on hydrothermal research appeared in 1845. It reports the successful synthesis of tiny quartz crystals upon transformation of freshly precipitated silicic acid in Papin's digestor by K. F. E. Schafthaul. The term hydrothermal usually refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions. Hannay (1880) claimed to have synthesized artificial diamond via hydrothermal method. Moreover, Moissan (1893) also claimed to have synthesized diamond artificially as large as 0.5 mm from charcoal. The first ever large size crystals obtained by the earliest workers was that of hydrated Potassium Silicate, which was about 2–3 mm long, by Friedel and Sarasin (1881). They termed their hydrothermal autoclave as hydrothermal bomb, because of the high pressure working conditions in their experiments. The first successful commercial application of hydrothermal technology began with mineral extraction or ore beneficiation in the 19th century. With the beginning of the synthesis of large single crystals of quartz by Nacken (1946) and zeolites by Barrer (1948), the commercial importance of the hydrothermal technique for the synthesis of inorganic compounds was realized.

2.2.3 Definition

In literature survey, there are different definitions suggested by many researchers for hydrothermal method. In 1913 Morey and Niggli defined "…in the hydrothermal method the components are subjected to the action of water, at temperatures generally near though often considerably above the critical temperature of water (~370°C) in closed bombs, and therefore, under the corresponding high pressures developed by such solutions " [68]. In Ref. [69] Laudise defined it as "hydrothermal growth means growth from aqueous solution at ambient or near-ambient conditions". Rabenau in 1985 defined hydrothermal synthesis as the heterogeneous reactions in aqueous media above 100°C and 1 bar [70]. Lobachev defined it as a group of methods in which crystallization is carried out from superheated aqueous solutions at high pressures [71]. According to Roy hydrothermal synthesis involves water as a catalyst and occasionally as a component of solid phases in the synthesis at elevated temperature (>100°C) and pressure (greater than a few atmospheres) [72]. Byrappa in 1992 defines hydrothermal synthesis as any heterogeneous reaction in an aqueous media carried out above room temperature and at pressure greater than 1 atm [71]. Yoshimura defined it as "…reactions occurring under the conditions of high-temperature–high-pressure (>100°C, >1 atm) in aqueous solutions in a closed system" [72]. With the vast number of publications under mild hydrothermal conditions in recent years, K. Byrappa in 2001 propose to define hydrothermal reaction as "any heterogenous chemical reaction in the presence of a solvent (whether aqueous or nonaqueous) above room temperature and at pressure greater than1 atm in a closed system." [73].

2.2.4 A reactant - Water

The performance of the solvent under hydrothermal conditions dealing with aspects like structure at critical, supercritical and sub-critical conditions, pH variation, viscosity, coefficient of expansion, density, etc. is to be understood with respect to pressure and temperature. Water is one of the most important solvent present in nature in plenty amount and has significant properties as a reaction medium under variable hydrothermal conditions. The biggest advantage of using water is the cheaper than other solvents, easily available and it can act as a catalyst for the synthesis of advanced materials by changing the temperature and the pressure. Water shows different characteristics under hydrothermal conditions than that of standard conditions. It is nontoxic, colorless, nonflammable, non-carcinogenic, non-mutagenic, and thermodynamically stable. Due to volatile nature, so it can be removed from the product very easily. Hydrothermal solvents have different properties at above 100^oC and above 1 atm, especially at critical point. In order to understand hydrothermal reactions the properties of solvent under hydrothermal conditions must be known very well.

At critical point, the solvents have different properties at above 100^oC and 1 atm, especially. To synthesize fine nanoparticles and to understand reactions the nature of solvent under hydrothermal conditions must be known very well. The solvent properties for many compounds, such as dielectric constant and solubility, change dramatically under supercritical conditions.

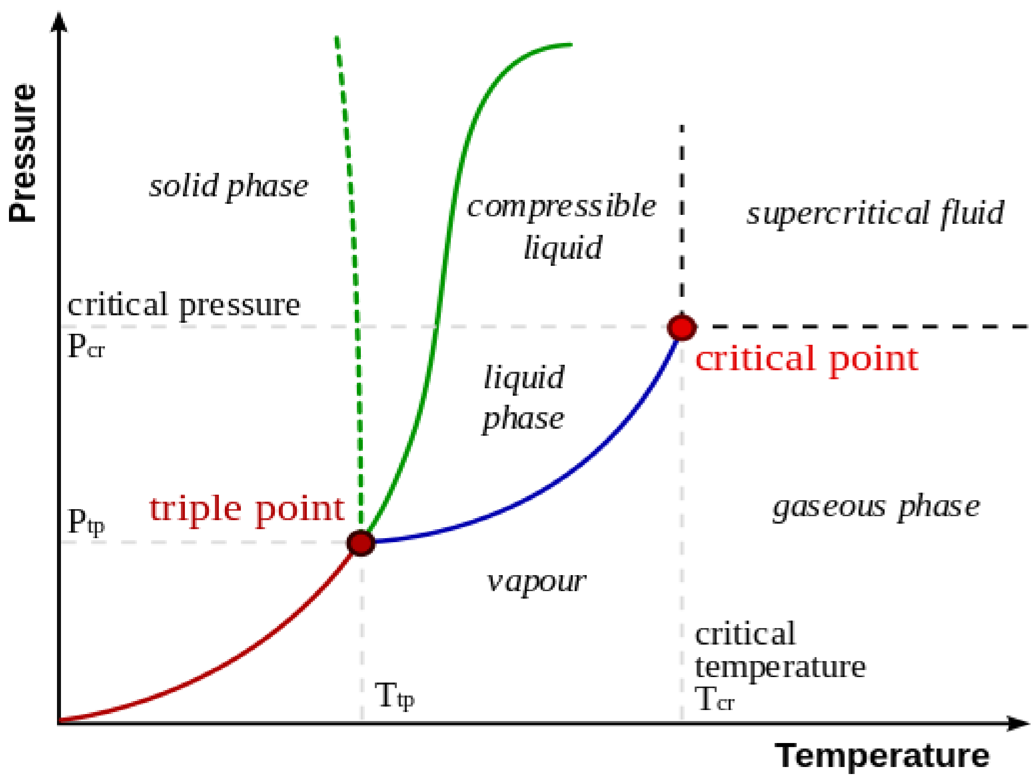

Figure 2.1 Phase diagram of water. [75]

In the Figure 2.1, the critical point marks the end of liquid-vapor coexistence curve at the critical temperature T_{cr}, and pressure, P_{cr}, in a phase diagram for a pure homogenous substance. The phase boundary between liquid and gas does not continue indefinitely. Instead, it terminates at a point on the phase diagram called the critical point. Above that, at extremely high temperatures and pressures, the liquid and gaseous phases become indistinguishable, is known as a supercritical fliud. It can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned"[76]. As the temperature increases, the liquid becomes less dense due to thermal expansion and at the same time the gas becomes denser. At the critical point the densities of both phases become the same. The compound is neither liquid nor gas any longer above the critical point, and it becomes supercritical fluid. After that, the phases of liquid and gas are not distinguishable and properties of SCF will be between gas and liquid. An outstanding feature of supercritical water as a particle formation medium is to control the crystal phase through adjustable solvent properties such as density of water. In addition, particle formation using supercritical water can reduce the alkaline concentration and keep it free of toxic organic solvents, thus, the hydrothermal process is compatible with green and sustainable chemistry in a way that reduces the environment load. We believe that transfer of supercritical hydrothermal technology of material production from research laboratory to industry will be achieved in the near future in combining commercial productivity and sustainable progress.

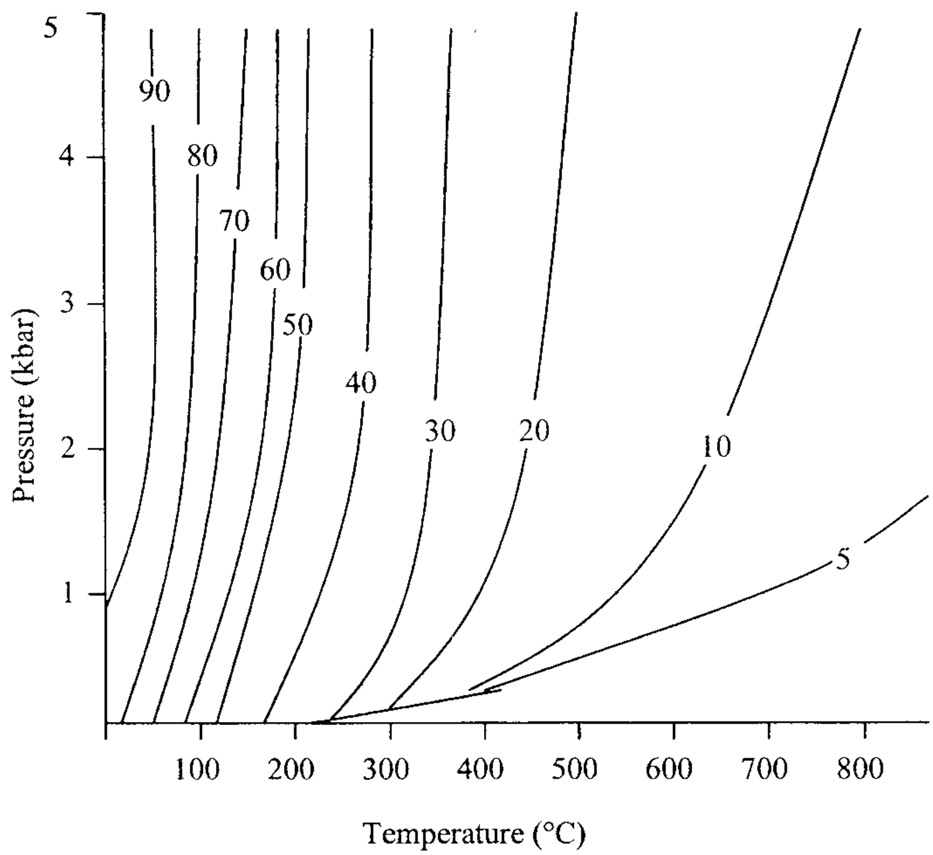

Figure 2.2 Variation of dielectric constant of water with temperature and pressure [77].

The dielectric constant that is defined as the ability of a solvent to charge separate increases sharply with the pressure in the compressible region that refers to the area around the critical point in which compressibility is considerably greater than would be forecasted from the ideal gas law. The dielectric constant of water decreases with increasing temperature and decreasing pressure. The dielectric constant is below 10 under supercritical conditions; the contribution of the dielectric constant to the reaction rates becomes remarkable based on the electrostatic theory [78]. Thus, supercritical water gives a favorable reaction field for particle formation, owing to the enhancement of the reaction rate and large super saturation based on the nucleation theory, due to lowering the solubility.

Another attractive feature of supercritical fluids is that the properties lie between that of gases and liquids. A supercritical fluid has densities similar to that of liquids, while the viscosities and diffusivities are closer to that of gases. Thus, a supercritical fluid can diffuse faster in a solid matrix than a liquid, yet possess a solvent strength to extract the solute from the solid matrix. [79] The transport properties diffusivity and viscosity that influence rates of mass transfer. Diffusivity is at least an order of magnitude higher and viscosity is lower compared with a liquid solvent. This means that diffusivity of reactants in SCF will occur faster than that in a liquid solvent, which means that solids can dissolve and migrate more rapidly in SCFs. High diffusivity, low viscosity and intermediate density of water increases the rate of the reaction. This behavior is also parallel to a change in density, as shown in Figure 2.2. Density changes sharply but continuously with pressure in the compressible region. One of the most important advantages of hydrothermal solvents is that a change in density affects the solvating power. A decrease in the density results in a significant change in solvating ability. If the density of water is high enough, nonpolar compounds may be completely miscible with it because water behaves as a non-aqueous fluid. Water is a polar solvent and its polarity can be controlled by temperature and pressure and this can be an advantage over other solvents.

2.2.5 Advantages and disadvantages of hydrothermal method

Hydrothermal synthesis offers several advantages over conventional and non-conventional bottom up approach. The hydrothermal synthesis method includes the ability to synthesize crystals of substances which are unstable near the melting point. It has ability to synthesize large crystals of high quality.

In Hydrothermal synthesis, reactions do not require much time compared to conventional methods. For instance, although a solid-state reaction can be performed in a few weeks hydrothermal reaction can be done in a few days. From the environmental viewpoint, hydrothermal methods are more environmentally favorable than many other methods. The low reaction temperatures also avoid other problems happened with high temperature processes (Czochralski method, Bridgeman method) such as poor stoichiometric control due to volatilization of components) and stress-induced defects (e.g. micro-cracks) caused by phase transformations that occur as the phosphor is cooled to room temperature. Moreover, the ability to precipitate the phosphor powders directly from solution regulates the rate and uniformity of nucleation, growth and aging, which affects size, morphology and aggregation control that is not possible with many synthesis processes [80].

It has rapid growth rates because of the rapid diffusion processes. The hydrothermal method is a growth technique from liquid solution, but the viscosity of the liquid is lower. Solubility of a liquid should be high for conventional methods or there will be a rate problem. Under hydrothermal conditions, diffusion is not a problem because of a low viscosity in comparison to viscosity at ambient temperature.Varieties of morphologies and particle sizes possible with hydrothermal processing. This method is useful to different industries which rely on powder (e.g. materials, pigments, pharmaceuticals, medical diagnostics) will benefit from having an access to powders with controlled size and morphology.

A main advantage of hydrothermal synthesis is that this method can be hybridized with other processes like microwave, electrochemistry, ultrasound, mechano-chemistry, optical radiation and hot-pressing. It enhances reaction kinetics and increase ability to make new materials. This simplistic method does not need any seed, catalyst, adverse and costly surfactant or template thus it is capable for large-scale and low-cost production with high-quality crystals. The unique pressure-temperature interaction of the hydrothermal solution allows the preparation of different phases, morphology of $CdWO_4$ phosphor that are difficult to prepare with other synthetic methods.

This route has several merits including simplicity, low processing temperatures, low cost, high product purity, and the ability to control the particle size [81]. Materials synthesized under hydrothermal conditions often exhibit differences in point defects when compared to materials prepared by high temperature synthesis methods. e.g. Tungstates of Ca, Ba, and Sr synthesized at room temperature by a hydrothermal method do not contain Schottky defects usually present in similar materials prepared at high temperatures [82] which results in improved luminescent properties. For long periods in synthesis, no chance to damage instrument so that no machining or treatment is needed after each experimental run.

The down side of this method is the high-pressure requirement and also difficulty on gathering data. Because of fast diffusion under hydrothermal conditions, super saturation occurs and results in dendritic growth that increases the chance of impurities and can reduce crystal quality. It has inability to monitor crystals in the process of their growth. A key limitation to the conventional hydrothermal method has been the need for time consuming empirical trial and error methods as a mean for process development.

2.3 Autoclave

Material processing under hydrothermal conditions requires a vessel capable of containing a highly corrosive solvent at high temperature and pressure [81]. Ideal hydrothermal apparatus popularly known as an autoclave should have the following characteristics:

1. Inert to acids, bases and oxidizing agents.

2. It should be easily assemble.

3. It should have sufficient length to obtain a desired temperature gradient.

4. It should be leak-proof at desired temperature and pressure.

5. It should bear high pressure and temperature for long duration of time.

Crystal growth under hydrothermal conditions requires a reaction vessel called an *autoclave*. In hydrothermal method highly corrosive salt are used to synthesis inorganic materials for longer reaction time. The Autoclave must be capable of sustaining highly corrosive solvent at high temperature and pressure for a longer duration of time. For selecting a suitable autoclave, the first and foremost parameter is the experimental temperature and pressure conditions and the corrosion resistance in that pressure-temperature range in a given solvent or hydrothermal fluid. In our case as the reaction is taking place directly in the vessel, the corrosion resistance is a prime factor in the choice of the autoclave material. The most successful corrosion resistant materials high-strength alloys, such as 316 series (austenitic) stainless steel, iron, nickel, cobalt-based super alloys, and titanium and its alloys. To avoid corrosion of autoclave material it should coated with non-reactive material called Teflon from inside. Due to the larger coefficient of thermal expansion of Teflon (the liner) versus metal (the material in which the liner is enclosed), the Teflon will expand and contract much more upon heating and cooling cycles than its enclosure material. We have designed teflon fitted stainless steel autoclave (figure 2.3).

Figure 2.3 Teflon fitted stainless steel autoclave.

2.4 Liners

Hydrothermal synthesis can be affected under temperatures and pressures below the critical point for a specific solvent above which differences between liquid and vapour disappear or under supercritical conditions [80]. The solubility of many oxides in hydrothermal solutions of salts is much higher than in pure water; such salts are called mineralizers. The mineralizer is highly corrosive and it can react with the vessel, which is inimical to obtaining high purity $CdWO_4$ crystals. It requires a suitable lining for the inner wall of the autoclave or separate liners placed in the autoclave. Hence, noble metal lining, liners, or capsules are used successfully for alkaline and neutral media. Studies related to reaction kinetics, solubility and materials processing under mild hydrothermal conditions or pressure temperature conditions below 250 bars and 300°C, teflon is the most popularly used lining material. Several new autoclave designs with Teflon lining or coating for such studies have been reported in literature. The teflon liner or beaker should sit exactly inside the autoclave without leaving any gap. As the temperature rises, the teflon expands and hermitic sealing can be obtained. The greatest disadvantages of teflon lining is that beyond 300°C, it cannot be used because teflon dissociates which affects the pH of neutral solutions. This coating tends to get torn and generally must be reapplied after few experiments. Detailed synthesis procedure is explained at the end of this chapter.

2.5 Effect of hydrogen

Hydrogen at high temperature and/or pressures can have a disastrous effect on alloys used in autoclaves [80]. It reduces the strength of the autoclaves through any one of the following processes: hydrogen embrittlement, irreversible hydrogen damage, or metal-hydride formation. These problems could be overcome through careful selection of alloys containing small additives such as Ti, Mo,V, heating in H_2 free atmosphere, and using alloys with low thermodynamic activity. Hydrogen is available from the water. Because the hydrogen atom is much smaller in size, it is able to migrate into the crystal lattice of Autoclave metal, and reside interstitially between the individual metal atoms. When these hydrogen atoms re-combine in voids of the metal matrix to form hydrogen molecules, they create pressure from inside the cavity they are in. This pressure can increase to levels where the metal has reduced ductility and tensile strength up to the point where it cracks called *hydrogen induced cracking*, or HIC.

2.6 Reagents and solvents

Cadmium Chloride ($CdCl_2$ .H2O), Sodium Tungstate (Na2WO_4.2H_2O) and Rare -earth Oxide are purchased from Alfa Aesar of A.R.(analytical reagent) grade and used without further purification. Distilled water was used as solvent to prepare all required solutions. Acetone and Ethanol were used to wash prepared samples.

2.7 Procedure

Cadmium Chloride ($CdCl_2$ .H2O), Sodium Tungstate (Na2WO_4.2H_2O) and Rare -earth Oxide were used as recieved without any further purification. Distilled water was used as a solvent to prepare all required solutions. Initially 30ml solution of 0.1M concentration of $CdCl_2$.H_2O was prepared by continuous stirring and 30 ml solution of 0.1M concentration of Na_2WO_4.2H_2O was added into it dropwise. To prepare sample, we added 30 ml solution of 0.01M concentration of Rare-earth Oxide.These precursors solutions were transferred to Teflon-lined stainless-steel autoclave having 90 ml capacity filled with reaction media up to 80% one by one. The autoclave was maintained at a temperature of 95^{0}C for 12 h and air cooled to room temperature. The prepared samples were washed several times with distilled water and lastly with absolute ethanol. Finally, a white powder was obtained after drying in vacuum at 80^{0}C for 2 h. Figure 2.4 shows the flow chart of undoped and Cerium doped $CdWO_4$ using the hydrothermal method.

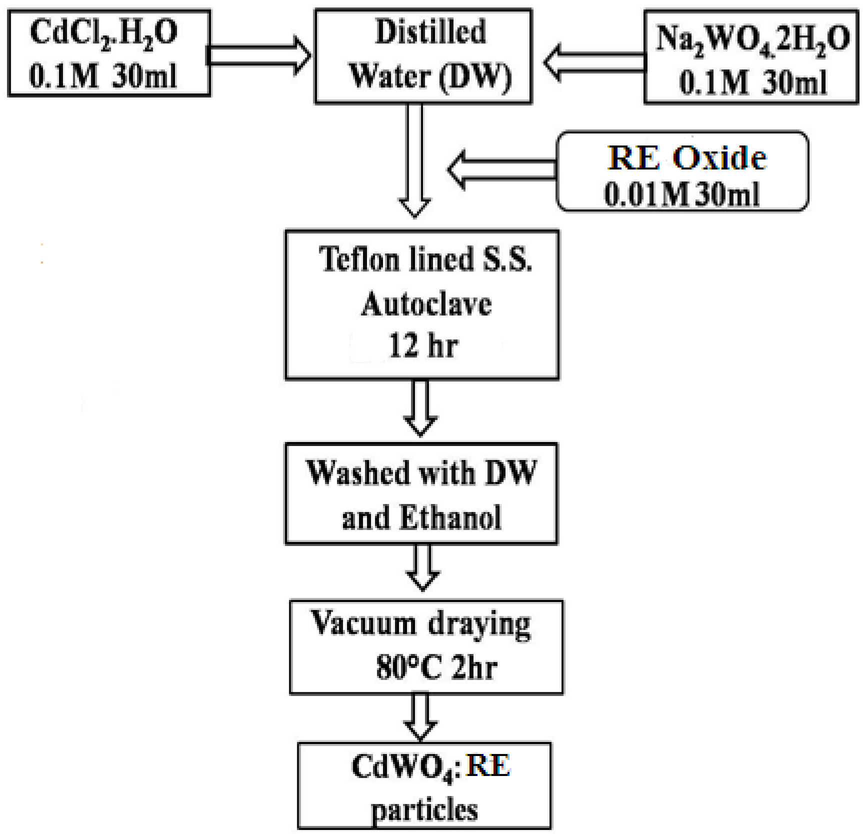

Figure 2.4 Flow chart of Hydrothermal Synthesis.

2.8 Summary of prepared samples

Undoped and doped $CdWO_4$ samples were prepared at different temperatures, pH and reaction time in order to study its effect on structural and optical properties. Summary of experiments performed during Ph.D. work is given in following tables.

Sr No.	Sample	Temperature(^{0}C)	Time(hr)	pH
1	$CdWO_4$	95	12	7
2	$CdWO_4$:Ce	95	12	7
3	$CdWO_{4:}$Er	100	12	7
4	$CdWO_4$:Nd	100	12	7
5	$CdWO_4$Ce+Nd	100	12	7
6	$CdWO_4$:Ce+Er	100	12	7
7	$CdWO_4$:Nd+Er	100	12	7
8	$CdWO_4$Ce+Nd+Er	100	12	7
9	$CdWO_4$	150	12	7
10	$CdWO_4$	100	12	7
11	$CdWO_4$:Ce	100	12	4
12	$CdWO_4$:Ce	100	12	6
13	$CdWO_4$:Ce	100	12	8
14	$CdWO_4$:Ce	150	12	4
15	$CdWO_4$:Ce	150	12	6
16	$CdWO_4$:Ce	150	12	8
17	$CdWO_4$:Ce	100	12	7
18	$CdWO_4$:Eu	150	12	4
19	$CdWO_4$:Eu	150	12	6
20	$CdWO_4$:Eu	150	12	8
21	$CdWO_4$:Eu	150	12	10

Table 2.1 List of Samples prepared by Hydrothermal Synthesis.

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