Chapter 2

Experimental Technique

Hydrothermal Method

2.1 History

The Hydrothermal Technique has been the most popular one, gathering interest from scientists and technologists of different disciplines, particularly in the last fifteen years. The word *"hydrothermal"* has geological origin. A self-explanatory word, "hydro" meaning water and "thermal" meaning heat. British Geologist, Sir Roderick Murchison (1792–1871) was the first to use this word, to describe the action of water at elevated temperature and pressure in bringing about changes in the earth's crust leading to the formation of various rocks and minerals [1]. The first publication on hydrothermal research appeared in 1845. This 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 using Hydrothermal Technique. Similarly, 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). Friedel and Sarasin (1881) termed their hydrothermal autoclave as *hydrothermal bomb,* because of the high pressure working conditions in their experiments.

2.2 Definitions

There are different definitions proposed by various scientists for hydrothermal method in literature. In 1913 Morey and Niggli defined hydrothermal synthesis as "...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 " [2]. In Ref. [3] 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 [4]. Lobachev defined it as a group of methods in which crystallization is carried out from superheated aqueous solutions at high pressures [5]. 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) [6]. Byrappa in 1992 defines hydrothermal synthesis as any heterogenous reaction in an aqueous media carried out above room temperature and at pressure greater than 1 atm [7]. Yoshimura in ref [8] defined it as "...reactions occurring under the conditions of high-temperature–high-pressure (>100°C, >1 atm) in aqueous solutions in a closed system". 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 than 1 atm in a closed system." [9].

2.3 Water as a Reaction Medium

Water is one of the most important solvent present in nature in abundant amount and has remarkable properties as a reaction medium under hydrothermal conditions. Water shows different characteristics under hydrothermal conditions than that of standard conditions. One of the biggest advantages of using water is the environmental benefit and cheaper than other solvents, and it can act as a catalyst for the formation of desired materials by tuning the temperature and the pressure. It is nontoxic, nonflammable, noncarcinogenic, nonmutagenic, and thermodynamically stable. Another advantage is that water is very volatile, so it can be removed from the product very easily.

Hydrothermal solvents have different properties at above 100°C 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.

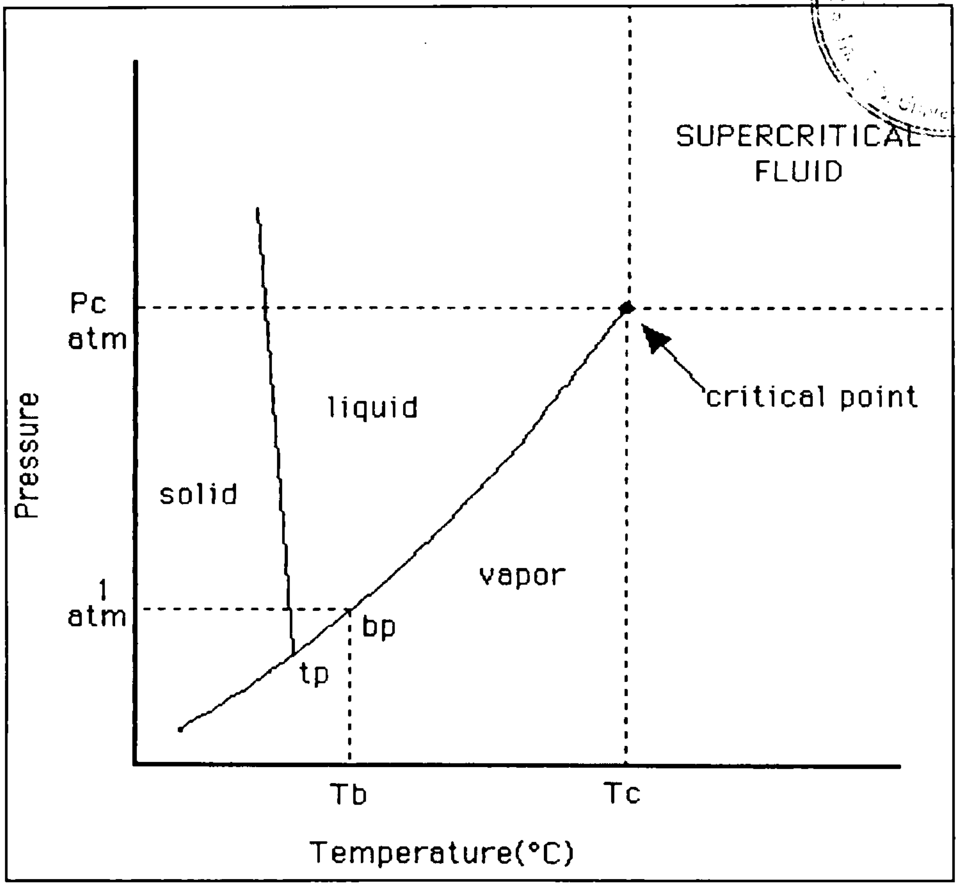

Figure 2.1 Phase diagram of water.

In the Figure 2.1, the critical point marks the end of liquid-vapor coexistence curve at the critical temperature, T_c, and pressure, P_c, in a phase diagram for a pure homogenous substance. A fluid is defined as being supercritical if it is maintained at conditions above its critical temperature and pressure. The properties of supercritical fluids (SCFs) vary depending on the pressure and temperature and frequently described as being intermediate between those of a gas and a liquid. 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.

Diffusivity and viscosity symbolizes transport properties 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.

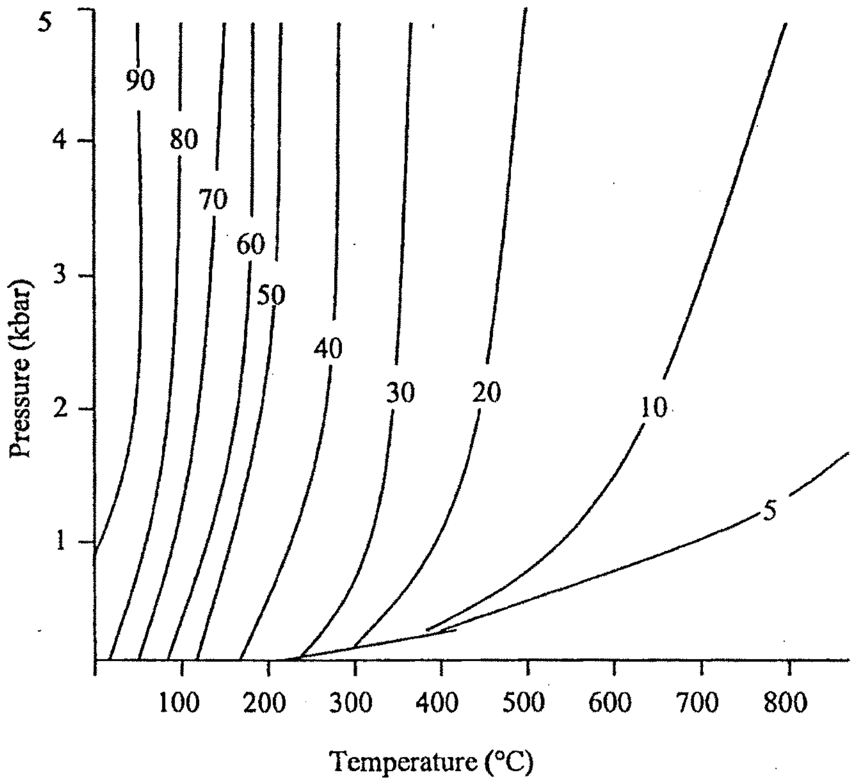

Figure 2.2 Variation of dielectric constant of water with temperature and pressure [10].

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. 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.

The physical and chemical properties of water and aqueous solutions in the temperature and pressure ranges required for hydrothermal synthesis have been discussed in numerous review articles and are well known. The PVT data for water up to 1000°C 10 kbar are known accurately enough (within 1% error) [11]. If the density of water is high enough, nonpolar compounds may be completely miscible with it because water behaves as a nonaqueous 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.

2.4 Merits of Hydrothermal Synthesis

Hydrothermal synthesis offers many advantages over conventional and non conventional synthesis methods. Unlike many advanced methods that can prepare a large variety of forms, the respective costs for instrumentation, energy and precursors are far less for hydrothermal methods. From the environmental perspective, hydrothermal methods are more environmentally benign than many other methods. The low reaction temperatures also avoid other problems encountered with high temperature processes (Czochralski method, Bridgeman method) such as poor stoichiometric control due to volatilization of components (e.g. volatilization PbO in $PbWO_4$) 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. Varities of morphologies and particle sizes possible with hydrothermal processing. This method is beneficial 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 for a wide range of reasons. The unique pressure-temperature interaction of the hydrothermal solution allows the preparation of different phases of $PbWO_4$ phosphor that are difficult to prepare with other synthetic methods. Phase fields are often simpler when hydrothermal solutions are used. 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 [12] which results in improved luminescent properties.

A major 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 to gain advantages such as enhancement of reaction kinetics and increase ability to make new materials. A great amount of work has been done to enhance hydrothermal synthesis by hybridizing this method with many other processes. This facile method does not need any seed, catalyst, harmful and expensive surfactant or template thus it is promising for large-scale and low-cost production with high-quality crystals.

2.5 Autoclave

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.

An ideal hydrothermal autoclave should have the following characteristics:

1. Inert to acids, bases and oxidizing agents.
2. It should be easily assemble and dissemble.
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.

2.6 Liners

In the hydrothermal experiments, the mineralizer used is highly corrosive and it can react with the vessel, which is inimical to obtaining high purity $PbWO_4$ 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.

We have designed a Teflon-lined stainless steel autoclave (Figure 2.3) having 90 mL capacity under the guidance of Prof. Diveker (retired Professor from IIT, Bombay) and with the help of Mr. Nitin (Technician, Chemical Engineering department, Faculty of Technology, The M.S.University of Baroda). This reaction vessel was coated with Teflon from inside and possesses a maximum operating temperature 200°C. To measure the temperature of reaction, Platinum Resistance Thermometer having range 0-200°C is used which is purchased by Cliff's Electronics, GIDC,Vadodara. In order to synthesis $PbWO_4$, mixture of Lead salt and Sodium Tungstate salt were taken in precise molar concentration and 80% filled of its maximum capacity in vessel reactor. Detailed synthesis procedure is explained at the end of this chapter.

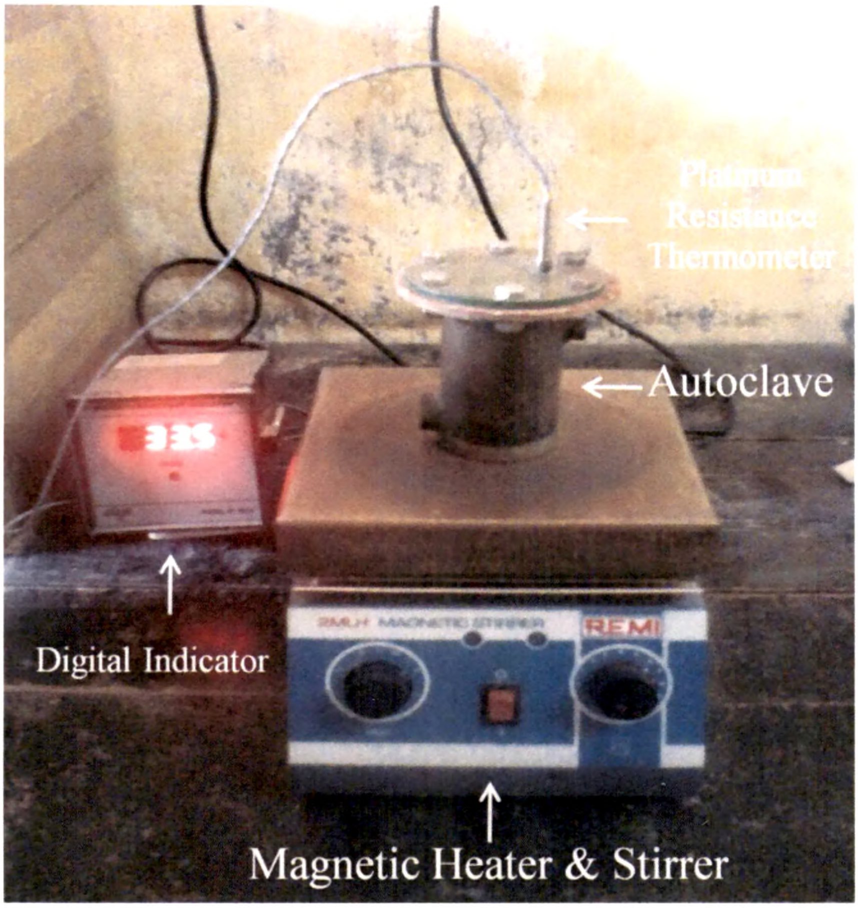

Figure 2.3 Teflon-Lined Stainless Steel Autoclave.

2.7 Effect of Hydrogen on Autoclave

Hydrogen at high temperature and/or pressures can have a disastrous effect on alloys used in autoclaves. 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.

2.7.1 Hydrogen embrittlement

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).

2.8 Synthesis

2.8.1 Reagents and Solvents

Lead sources [e.g. $PbCl_2$, $Pb(NO_2)_3$ or $Pb(CH_3COO)_2$] , $Na_2WO_4\cdot 2H_2O$ and CeO_2 chemicals 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.

2.8.2 Procedure

Hydrothermal method used to prepare $PbWO_4$ as well as Cerium doped $PbWO_4$ nanomaterials with different morphologies are explained here. To produce $PbWO_4$ or $PbWO_4$:Ce, we require different Lead sources [e.g. $PbCl_2$, $Pb(NO_2)_3$ or $Pb(CH_3COO)_2$] , $Na_2WO_4\cdot 2H_2O$ and CeO_2. All the lead sources are well soluble in distilled water. Initially 30 ml solution of 0.01 M concentration of PbX_2 [where X= Cl, NO or CH_3COO] was prepared in distilled water. To prepare 0.01 M concentration of PbX_2 solution 0.08343 g of $PbCl_2$, 0.0993g of $Pb(NO)_2$ or 0.1138g of $Pb(CH_3COO)_2$ is poured in a beaker containing 30ml distilled water with continuous stirring on Magnetic stirrer and Heater. Similarly 30 ml solution of 0.01 M (0.0989 g) concentration of Na_2WO_4 was added in it. Instantly precipitates of $PbWO_4$ were produced. To prepare Cerium doped $PbWO_4$ 0.001 M (0.005136 g) concentration of CeO_2 was added into previously prepared solution. The resulting precursor suspension was transferred to Teflon lined stainless steel autoclave of 90 ml capacity filled 80% with reaction media (i.e. distilled water) one by one. Then the autoclave was maintained at desired temperature and duration. After achieving required temperature and time for reaction autoclave is air cooled to room temperature. Obtained precipitates were washed and filtered several times with distilled water by using Wattman fine filter papers to remove salt which is produced during reaction. As obtained white precipitates were washed several time with absolute ethanol. To remove water content white powder was dried in vacuum Oven at 80°C for 2h. To understand above procedure simple flow chart is shown in Figure 2.4.

Hydrothermal Synthesis of Ce doped $PbWO_4$

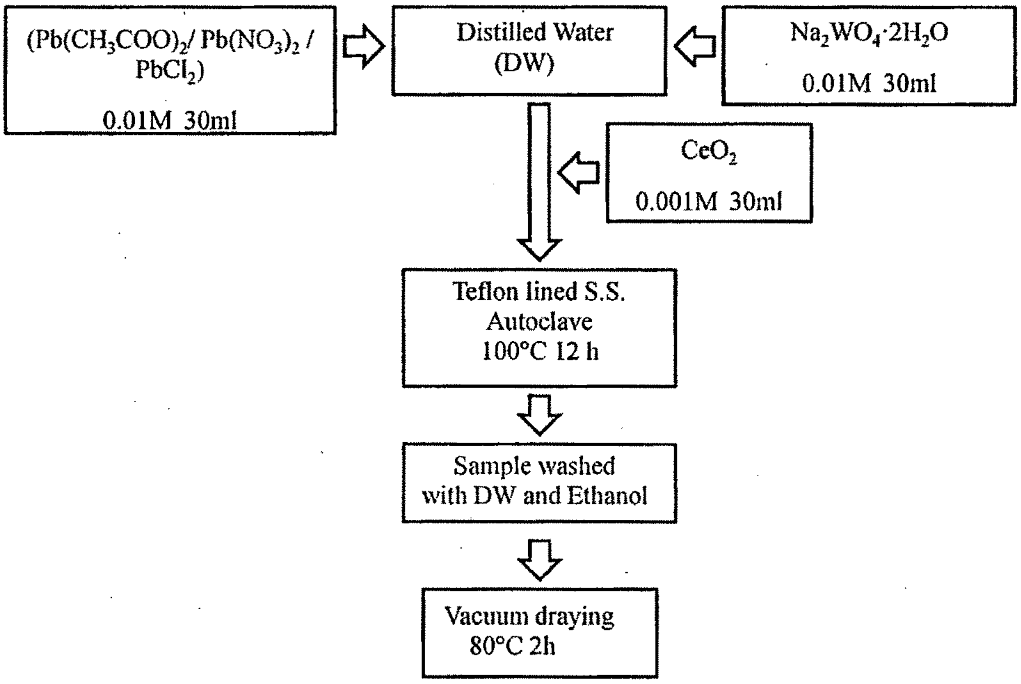

Figure 2.4 Flow chart of Hydrothermal Synthesis

2.9 Summary of Prepared Samples

We have synthesized undoped and Cerium doped $PbWO_4$ at different temperatures, with different Lead salts and Cerium concentrations (in molar), at different 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.

Table 2.1 $PbWO_4$ and $PbWO_4$:Ce prepared with different Lead Sources

Sample	Reagent1 conc. (0.01M)	Reagent2 conc. (0.01M)	Dopent conc. (0.001M)	Solvent	Temp. (°C)	Time (h)
1	$Pb(CH_3COO)_2$	Na_2WO_4	-	D.W.	100	12
2	$Pb(CH_3COO)_2$	Na_2WO_4	CeO_2	D.W.	100	12
3	$Pb(NO_3)_2$	Na_2WO_4	-	D.W.	100	12
4	$Pb(NO_3)_2$	Na_2WO_4	CeO_2	D.W.	100	12

Table 2.2 $PbWO_4$ and $PbWO_4$:Ce prepared at different reaction conditions using Lead Chloride as a Lead Source

Sample No.	$PbCl_2$ conc. (M)	Na_2WO_4 conc. (M)	Ce conc. (M)	Temp. (°C)	Time (h)	pH
5	0.01	0.01	-	100	10	7
6	0.01	0.01	0.001	100	10	7
7	0.01	0.01	-	125	10	3
8	0.01	0.01	-	125	10	7
9	0.01	0.01	-	125	10	11
10	0.01	0.01	-	150	10	7
11	0.01	0.01	0.001	150	10	7
12	0.01	0.01	-	200	10	7
13	0.01	0.01	0.001	200	10	7
14	0.01	0.01	0.001	R.T.	10	7

2.9 Characterization

Powder X-ray diffraction (XRD) patterns of $PbWO_4$ samples which are tabulated in Table 2.1 were recorded at ERDA, Vadodara with a Japan Rigaku D/max-RB diffractometer at a scanning rate of 3°/min using Cu Kα radiation (λ= 0.15406 nm). XRD measurements of $PbWO_4$ samples which are tabulated in Table 2.2 were carried out using Bruker D8 Advance X-ray diffractometer at UGC-CSR Indore Center. X-rays were produced using a sealed tube and the wavelength of x-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye detector). Morphology of as-prepared samples was studied with JEOL JSM-6380LV scanning electron microscopy (FESEM) at ERDA. The microstructure and surface morphology of the microcrystalline powders were observed by transmission electron microscopy (TEM, Tecnai 20 G2 FEI made) at UGC-CSR Indore Center and at SICART, Vidhyanagar. The photoluminescence (PL) of all the samples were investigated on a Shimadzu spectrofluorophotometer at room temperature with Xenon lamp as excitation source at Applied Physics Department, M.S.University of Baroda.

References

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