CHAPTER 1

INTRODUCTION

1.1 Introduction

Nanocrystals of metals, oxides and semiconductors have been intensely studied for several years by different chemical and physical methods [1]. But the chemical methods are rather predominant compared with cutting or reshaping processes, physical methods [2]. In the past decade, the realization that electronic, optical, magnetic and chemical properties of nanocrystals were influenced by their sizes, which has motivated intense research in this area. The past couple of years seemed to be on high activity in this area, driven by advances such as the ability to synthesize nanocrystals of different shapes [1].

A narrow definition of nanostructures is that they include structures with at least two dimensions below 100 nm. An extended definition also includes structures with one dimension below 100 nm and a second dimension below 1 μm. Among these nanomaterials include zero-dimensional nanomaterials, one- dimensional nanowires and nanotubes and two- dimensional nanofilms and nanowalls. The nano-sizes improve some properties of the nanomaterials, because they have more surface area. Thus, they have higher efficiency novel luminescent materials, catalyst and super high density information storage. Nowadays, they have been studied intensely in the last several years due to their importance in fundamental research and potential application in fabricating electronic, optoelectronic, and sensing devices [1-3].

Properties of such nanomaterials are strongly dependant on their size and shape. The control of the morphology of inorganic materials has rapidly developed into a promising field in materials chemistry because the physical and chemical properties of nanomaterials depend not only on their composition but also on their structure, phase, shape, size and size distribution, and synthesis forming of essential component of nanomaterials and nanotechnology. Comparing to nanomaterials generated by physical methods such as laser ablation, arc-discharge and evaporation, the chemical methods have proved to be more effective by providing better control their different size, shapes and others [1-3].

Chemical synthesis of nanomaterials has been reviewed by a few authors, but innumerable improvements and better methods are being reported continually in the last few years because the emphasis of research had led to the development of many synthetic routes for the controllable synthesis of ordered structures. In general, rare earth phosphates have been prepared by solid state reactions and aqueous reactions. In solid state reactions, high reaction temperature, and long heating time are required to obtain a pure phase of the multicomponent particles. Then, a number of attempts have been made to develop the preparation of rare earth phosphates by applying soft solution method. This method has been widely used as one of the most effective approaches owing to availability of flexible adjustment of the experimental parameters of the synthetic system. The concepts of this method are to realize the low energy and low waste process for inorganic materials. Soft solution process means to fabricate shaped, sized and controlled advanced materials from aqueous solutions without excess heat, energy consumption, expensive equipment and precursor, that is, one of the most economically and environmentally friendly preparation techniques for advanced materials. With this method, fabrication of various materials with the minimum amount of raw material resources by a single synthetic step at low energy can be realized [4].

Although, the hydrothermal/solvothermal method is one of the most promising solution techniques for preparation of rare earth phosphates with controlled size and shape. But, the microwave irradiation is also a candidate in the synthesis of rare earth phosphates due to rapid volumetric heating, fast reaction rate, short reaction time, and energy saving. Comparing with the conventional solid state reaction, solution-based synthesis results in higher levels of chemical homogeneity. Also, mixing of the starting materials at the molecular level is achieved in solution-based systems; this is especially important when rare earth phosphates are being prepared [5].

It is well known that the morphology and size affect to the luminescent properties of the phosphor materials. So, the scientists and researchers have been developed the phosphor materials to be in the nanoscale. In the last several years, various methods have been used to control the morphology and size of products such as adding template/surfactant, controlling temperature, pH value, reaction time, starting material and so on [1-3].

1.2 Rare earth elements (REE) [6-7]

The rare earth elements are also known as the lanthanide series of elements and include lanthanum, cerium and 13 elements in the lanthanide series of the Periodic Table of the Elements. The better-known elements are cerium, lanthanum, neodymium, praseodymium, gadolinium, europium, and samarium. The rare earths share many common properties and occur together in natural conditions. It is quite difficult to disintegrate or even distinguish them from each other. There are very little differences in solubility and complex formation between them. The rare earth metals naturally occur together in minerals: monazite is a mixed rare earth phosphate.

The elements range in crustal abundance from cerium, the 25th most abundant element of the 78 common elements in the Earth's crust at 60 parts per million, to thulium and lutetium, the least abundant rare-earth elements at about 0.5 part per million. The elemental forms of rare earths are iron gray to silvery lustrous metals that are typically soft, malleable, ductile and usually reactive, especially at elevated temperatures, and they have high electrical conductivity.

Rare earths are found with non-metals, usually as the 3+ oxidation state. There is little tendency to vary the valence. Europium also has a valence of 2+ and cerium a valence of 4+.

The rare earths' unique properties are used in a wide variety of application, from everyday household items, such as rechargeable batteries to cutting-edge technologies such as super alloys used in the aerospace industry. Their most important commercial-grade end-uses are petrochemical sector, electronics, glass, ceramic industry, and metallurgy.

About 30% of the rare earths produced are used as catalysts in the petroleum and automotive industries, as shown in figure 1.1. For example, cerium is a critical component in both gasoline and the newer diesel catalytic converters found on automobiles and trucks. Among other things, the cerium protects the platinum group metals in the converter from oxidation. Demand for REE for catalysts production steadily increases.

The greatest REE end-use in money terms is production of luminophors (the greatest market of yttrium, europium and terbium), which are used in TV, computers, screens, compact lamps, etc. This sector also promises stable growth of demand for REE. Cerium compounds are applied as polishing powders for lenses, mirrors and cathode ray tubes. A new market became use of polishing powders for mechanical-chemical polishing microchips: this segment demonstrates now above 50% annual growth. One more REE end-use is NiMH batteries, which are the battery of choice for many hybrid vehicles, and demand for these batteries is expected to grow with the demand for hybrids.

An important REE market in developed countries is production of commercial electrical and electronic ceramics (capacitors, filters, etc.), founded growing demand at present time.

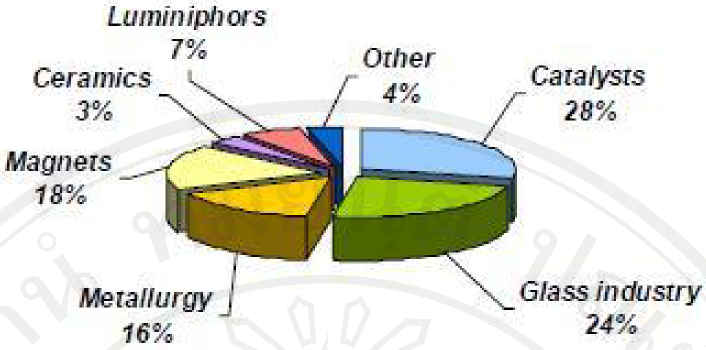


Figure 1.1 Pattern of world consumption of Rare earth elements (REE) [6].

1.3 Lanthanide phosphate ($LnPO_4$; Ln = La, Ce)

In recent years, much interest has been focused on the synthesis and luminescence of nano-sized lanthanide orthophosphates for their potential application in optoelectronic devices and biological fluorescence labeling. $LnPO_4$ and its solid solutions can be used in luminescent lamps as a highly efficient emitter [8].

Moreover, rare-earth orthophosphates are a very interesting class of host lattices for activator ions due to their physical and chemical inertness (high insolubility, stability against high temperatures or against high energy excitations), thus providing durable phosphors. These materials can present high excitabilities in the vacuum ultraviolet region (VUV, at ~170 nm),which enables the main applicability in plasma display panels (PDPs) and in new generation fluorescent lamps (without mercury) [9].

1.3.1 Structure

$LnPO_4$ can be divided into two groups with different crystal structure.

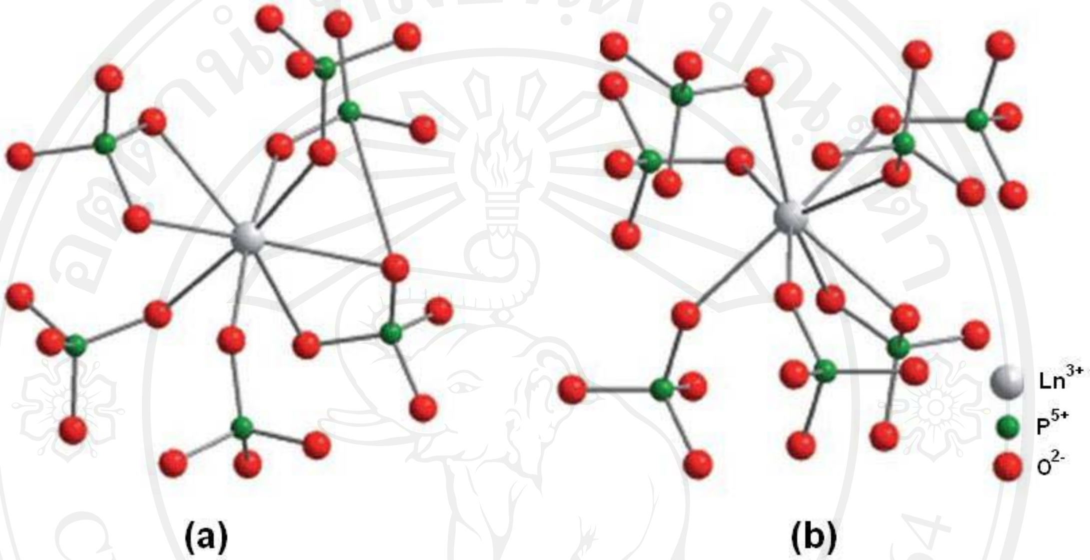


Figure 1.2 View of the $LnPO_4$ structures in: (a) the hexagonal phase and (b) the monoclinic phase, showing the connection of the cerium atom to the PO_4^{3-} tetrahedron [8].

According to the crystal structures of the hexagonal and monoclinic, as shown in figure 1.2, it could be found that the Ln atoms in the two structures are surrounded by different number of PO_4^{3-} tetrahedrons. In the hexagonal $LnPO_4$, the Ln atom connects six tetrahedral PO_4^{3-}, while the Ln atom connects seven tetrahedral PO_4 in the monoclinic $LnPO_4$. Obviously, to form monoclinic $LnPO_4$, the Ce atom need connecting with more PO_4^{3-} and high PO_4^{3-} concentration might be beneficial for its crystallization [8].

Moreover, hexagonal phase could be easily obtained at low temperature, and the corresponding nanorods/nanowires with a variable size have been hydrothermally synthesized. Monoclinic phase generally exists as natural monazite, bulk materials of which could be prepared via the solid state reaction and hydrothermal method at high temperature [8].

1.3.2 Photoluminescence properties

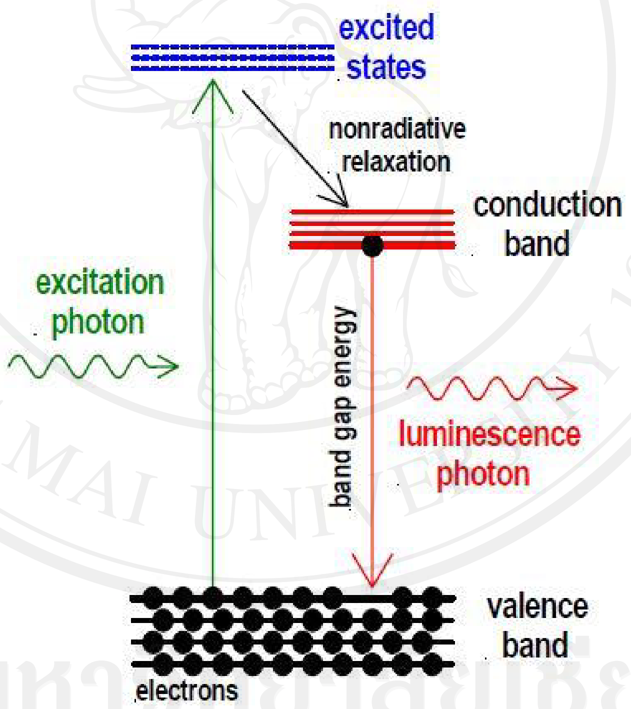


Figure 1.3 The process of photon excitation followed by photon emission is called photoluminescence [10].

All solids including semiconductors have so-called "energy gaps" for the conducting electrons. In order to understand the concept of a gap in energy, first consider that some of the electrons in a solid are not firmly attached to the atoms, as they are for single atoms, but can hop from one atom to another. These loosely attached electrons are bound in the solid by differing amounts and thus have much different energy. Electrons having energies above a certain value are referred to as conduction electrons, while electrons having energies below a certain value are referred to as valence electrons. This is shown in the diagram where they are labeled as conduction and valence bands. The word band is used because the electrons have a multiplicity of energies in either band. Furthermore, there is an energy gap between the conduction and valence electron states. Under normal conditions electrons are forbidden to have energies between the valence and conduction bands [10-11].

If a light particle (photon) has energy greater than the band gap energy, then it can be absorbed and thereby raise an electron from the valence band up to the conduction band across the forbidden energy gap, as shown in figure 1.3. In this process of photoexcitation, the electron generally has excess energy which it loses before coming to rest at the lowest energy in the conduction band. At this point the electron eventually falls back down to the valence band. As it falls down, the energy it loses is converted back into a luminescent photon which is emitted from the material. Thus the energy of the emitted photon is a direct measure of the band gap energy (E_g). The process of photon excitation followed by photon emission is called photoluminescence [10].

When the light emission by lanthanide ions is discussed, one often uses the term “luminescence”, rather than the terms “fluorescence” or “phosphorescence”. The reason is that the terms fluorescence and phosphorescence are used to describe light emission by organic molecules and that these terms incorporate information on the emission mechanism: fluorescence is singlet-to-singlet emission (i.e., a spin-allowed transition) and phosphorescence is triplet-to-singlet emission (i.e., a spin-forbidden transition), as shown in figure 1.4 [11].

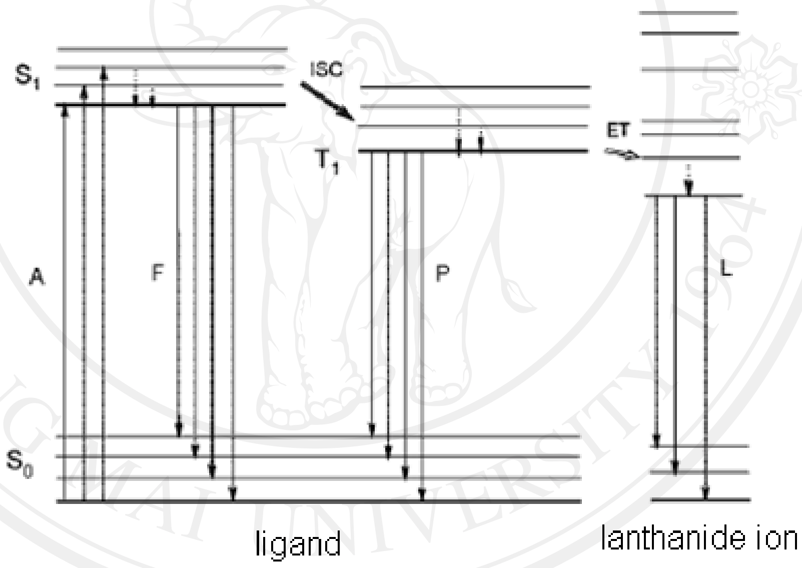


Figure 1.4 Schematic representation of photophysical processes in lanthanide(III) complexes (antenna effect). Abbreviations: A) absorption; F) fluorescence; P) phosphorescence; L) lanthanide-centered luminescence; ISC) intersystem crossing; ET) energy transfer; S) singlet; T) triplet. Full vertical lines indicate radiative transitions; dotted vertical lines indicate nonradiative transitions [11].

.

In the case of the lanthanides, the emission is due to transitions inside the 4f shell, thus intraconfigurational f-f transitions. Because the partially filled 4f shell is well shielded from its environment by the closed $5s^2$ and $5p^6$ shells, the ligands in the first and second coordination sphere perturb the electronic configurations of the trivalent lanthanide ions only to a very limited extent. This shielding is responsible for the specific properties of lanthanide luminescence, more particularly for the narrowband emission and for the long lifetimes of the excited states.

The trivalent ions of the lanthanide series are characterized by a gradual filling of the 4f orbital, from $4f^0$ (for La^{3+}) to $4f^{14}$ (for Lu^{3+}). One of the most interesting features of these ions is their photoluminescence. Several lanthanide ions show luminescence in the visible or near-infrared spectral regions upon irradiation with ultraviolet radiation.

The color of the emitted light depends on the lanthanide ion. For instance, Eu^{3+} emits red light, Tb^{3+} green light, Sm^{3+} orange light, and Tm^{3+} blue light. Yb^{3+}, Nd^{3+}, and Er^{3+} are well-known for their near-infrared luminescence, but other lanthanide ions (Pr^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, and Tm^{3+}) also show transitions in the near-infrared region. Gd^{3+} emits in the ultraviolet region, but its luminescence can only be observed in the absence of organic ligands with low-lying singlet and triplet levels.

Ce^{3+} is a special case because this ion emits intense broadband emission due to allowed f-d transitions. The position of the emission maximum strongly depends on the ligands environment of the Ce^{3+} ion. Depending on the method of excitation, different types of luminescence are defined, for example, photoluminescence (emission after excitation by irradiation with electromagnetic radiation), electroluminescence (emission by recombination of electrons and holes under the influence of an electric field), chemiluminescence (nonthermal production of light by a chemical reaction), or triboluminescence (emission observed by applying mechanical stress to crystals or by fracture of crystals) [10-13].

1.3.3 Application [11]

a) Luminescent Thin Films : Thin transparent polymer films of poly(vinyl chloride) or polyethylene find widespread use in agriculture and horticulture as covers for hotbeds and greenhouses to protect the plants from low temperatures or damage by intense UV radiation. It has been proposed to add luminescent molecular lanthanide complexes or lanthanide-doped inorganic compounds to such polymer films. The luminescent compounds can absorb the UV part of the solar spectrum and transform it into visible light. The absorption of UV radiation protects the polymer films against photodegradation and makes it possible to convert a part of the solar spectrum that cannot be used for photosynthetic processes into wavelengths that can be absorbed by the chlorophyll molecules in plants. The doping of luminophores into the films has thus a double advantage: (1) stabilization of the polymer films so that their service life will be extended and (2) a more efficient use of solar energy.

b) Lasers : The possibility to use lanthanide complexes for the design of lasers gave a strong impulse to the spectroscopic study of these complexes in the early 1960s. In order to achieve uniform excitation of the solutions containing the lanthanide chelate at the concentration required for laser action, only thin samples could be used. Therefore, most of the studies of liquid lasers have been performed on laser solutions in a capillary tube or on lanthanide doped polymers drawn to fibers.

c) LEDs : Light emitting diodes (LEDs) will probably become the most important type of light source for artificial lighting in the 21^{st} century and will probably replace the incandescent lamps and even the mercury-containing discharge lamps. Typically, a LED consists of inorganic p- and n-type semiconductors. The holes and electrons are driven to the p-n junction by the applied electric field. The electrons and holes recombine at this p-n junction, and the excess of energy is emitted as visible or infrared radiation. In a LED, electrical energy is transformed into light (electroluminescence). In organic light emitting diodes (OLEDs), the active components are organic molecules instead of inorganic semiconductors. OLEDs are mainly developed for display applications. One hopes to use OLEDs for the design of large flat panel displays with very wide viewing angles. The advantages of OLEDs are that they are easier and cheaper to fabricate than their inorganic counterparts, that they can be made very large (luminescent sheets), and that they can be deposited on almost every substrate including flexible ones, like plastics, to yield flexible displays. In theory, incorporation of lanthanide complexes in the emitting layer of OLEDs offers two main advantages: (1) improved color saturation and (2) higher efficiency of the OLED. Because of the sharp emission bands of the trivalent lanthanide ions (with a full-width at half-maximum of less than 10 nm), lanthanide luminescence is highly monochromatic. These results are much better color saturation than when organic molecules are used as the emissive materials.

1.4 Microwave irradiation method

1.4.1 Microwave irradiation [14-17]

Development of new routes for the synthesis of solids is an integral aspect of materials chemistry. Some of the important reasons for this are the continuing need for fast and energy-efficient techniques, necessity to avoid competing reactions in known processes, and the challenge implied in the synthesis of metastable phases by passing thermodynamically reversible routes. The microwave assisted route is yet another novel method of synthesis and is a very rapid in the developing area of research.

The developing of microwave technology was stimulated by World War II, when the magnetron was designed to generate fixed frequency microwaves for RADAR devices. Percy Le Baron Spencer of the Raytheon Company accidentally discovered that microwave energy could cook food when a candy bar in his pocket melted while he was experimenting with radar waves. Further investigation showed that microwave could increase the internal temperature of food much quicker than a conventional oven. This ultimate led to the introduction of the first commercial microwave oven for home use in 1954. Investigation into the industrial applications for microwave energy has found many used including irradiating coal to remove sulfur and other pollutant, rubber, vulcanization, product drying, moisture and fat analysis of food products and solvent extraction application.

Microwaves are a powerful, reliable energy source that may be adapted to many applications. Understanding the basic theory behind microwaves will provide the organic chemist with the right tools and knowledge to be able to effectively apply microwave energy to any synthetic route.

A microwave is a form of electromagnetic energy between infrared waves and radio waves, whose wavelengths lie in the range of 0.01 to 1 meter (frequency range of 0.3 to 300 GHz), as shown in Figure 1.5. Within this region of electromagnetic energy, only molecular rotation is affected, not molecular structure. A large part of the microwave spectrum is used for communication purposes and only narrow frequency windows centered at 900 MHz and 2.45 GHz are allowed for microwave heating purposes. However, for their use in laboratory reactions, a frequency of 2.45 GHz is preferred, since this frequency has the right penetration depth to interact with laboratory reaction conditions. Beyond 30 GHz, the microwave frequency range overlaps with the radio frequency range. The microwave electromagnetic spectrum is divided into sub-bands comprising the following frequency ranges (Table 1.1). While the lower microwave frequency ranges (L band) are used for the purpose of communication, the higher frequency ranges (W band) in the spectrum are used for analytical techniques such as spectroscopy. Microwave RADAR equipment that operate at lower wavelengths (0.01-0.25 m) are used for communication [15].

Table 1.1 Microwave Frequency Bands.

BANDS	**FREQUENCY**
L	1-2 GHz
S	2-4 GHz
C	4-8 GHz
X	8-12 GHz
Ku	12-18 GHz
K	18-26 GHz
Ka	26-40 GHz
Q	30-50 GHz
U	40-60 GHz
V	46-56 GHz
W	56-100 GHz

Microwave energy, Figure 1.6, consists of an electric field and a magnetic field, though only the electric field transfers energy to heat a substance. Magnetic field interactions do not normally occur in chemical synthesis. Microwave move at the speed of light (300,000 km/sec). Thus, microwave will not affect the structure of a molecule. In the excitation of molecules, the effect of microwave absorption is purely kinetic.

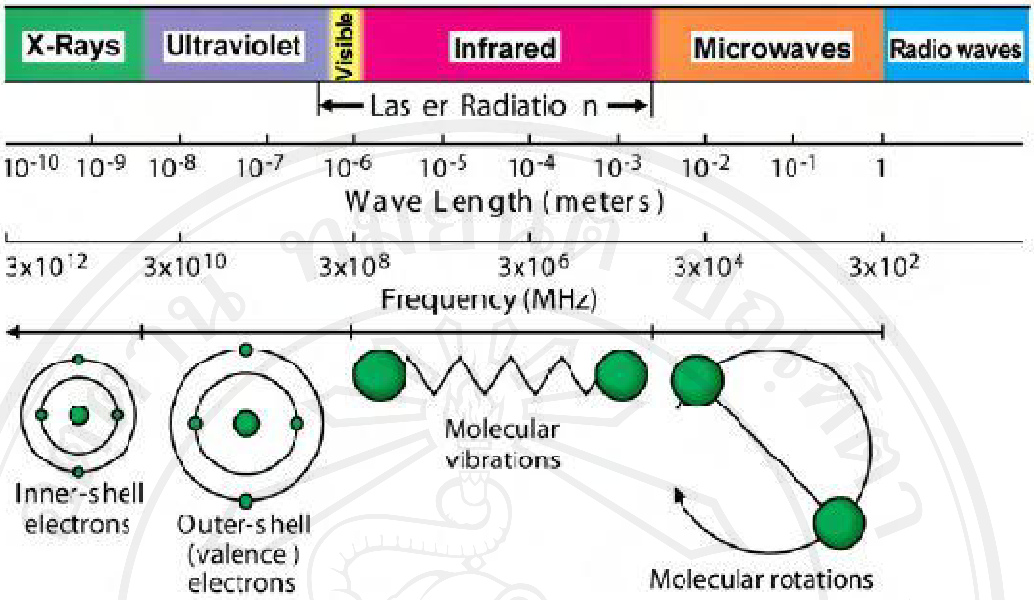


Figure 1.5 The electromagnetic spectrum.

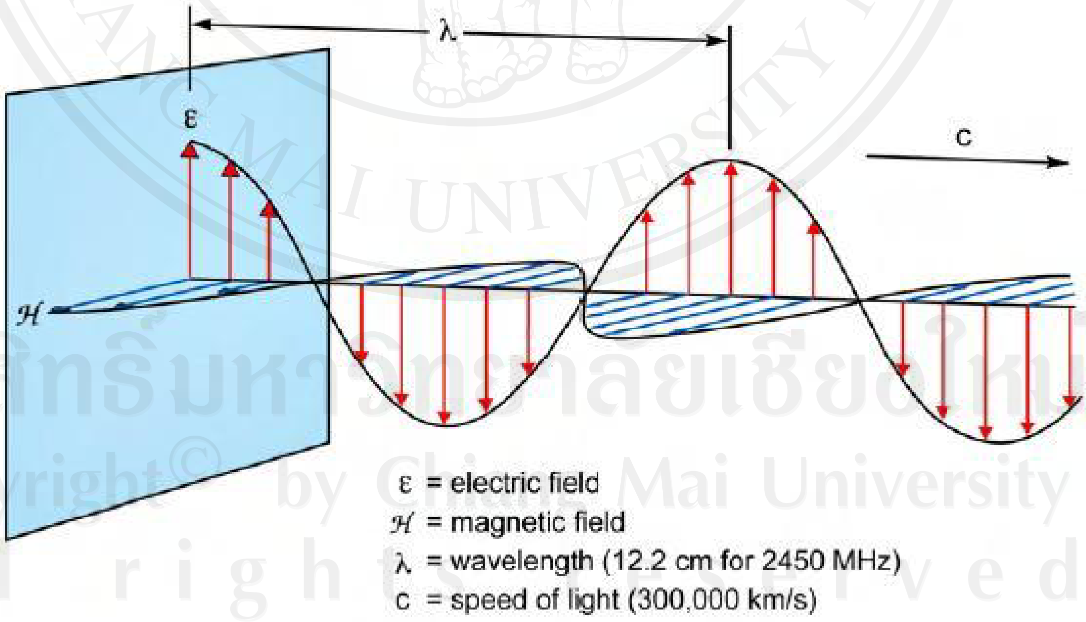
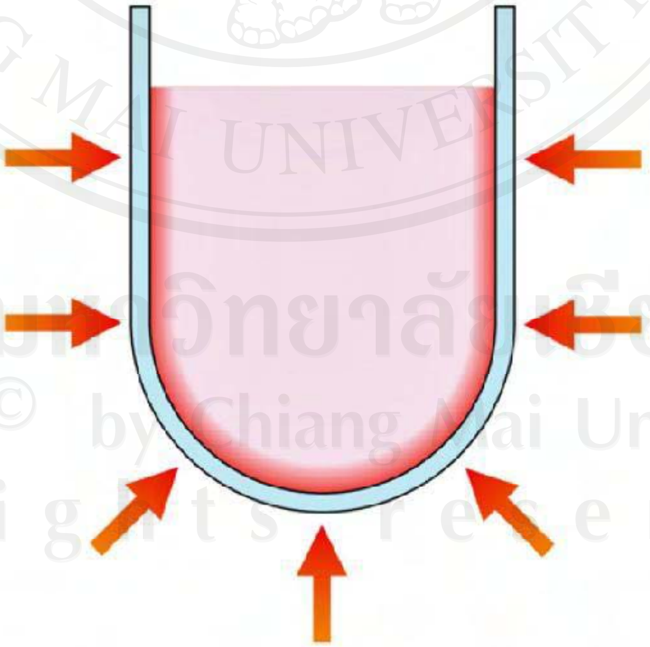


Figure 1.6 A microwave.

1.4.2 Microwave heating

Traditionally, chemical synthesis has been achieved through conductive heating with an external heat source. Heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and reactants (Figure 1.7). This is a slow and inefficient method for transferring energy into the system because it depends on the thermal conductivity of the various materials that must be penetrated. It results in the temperature of the vessel being higher than that of the reaction mixture inside until sufficient time has elapsed to allow the container and contents to attain thermal equilibrium. This process can take hours. Conductive heating also hinders the chemist's control over the reaction. The heat source must physically be removed and cooling administered to reduce the internal bulk temperature.



Temperature on the outside surface is greater than the internal temperature.

Figure 1.7 Schematic of sample heating.

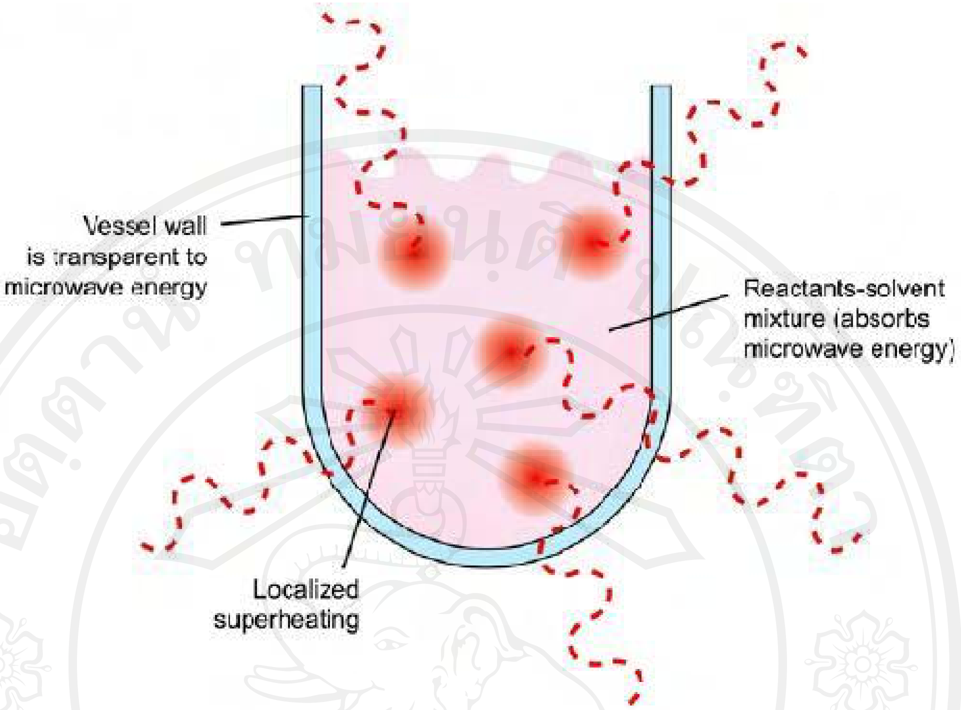


Figure 1.8 Schematic of sample heating by microwaves.

Microwave heating, on the other hand, is very different process. As shown in Figure 1.8, the microwaves couple directly with the molecules that are present in the reaction mixture, leading to a rapid rise in temperature. Because the process is not dependent upon the thermal conductivity of the vessel materials, the result is an instantaneous localized superheating of anything that will react to either dipole rotation or ionic conduction, the two fundamental mechanisms for transferring energy from microwaves to the substance being heated. Microwaves heating also offers facile reaction control. It can be described as "instant on-instant off". When the microwave energy is turned off, latent heat is all that remains.

Dipole rotation is an interaction in which polar molecules try to align themselves with the rapidly changing electric filed of the microwave. The rotational motion of the molecule as it tries to orient itself with the filed results in a transfer of energy. The coupling ability of this mechanism is related to the polarity of the molecules and their ability to align with the electric field. There are a number of factors that will ultimately determine the dipole rotation coupling efficiency; however, any polar species (solvent and/or substrate) that are present will encounter this mechanism of energy transfer.

The second way to transfer energy is ionic conduction, which results if there are free ions or ionic species present in the substance being heated. The electric field generates ionic motion as the molecules try to orient themselves to the rapidly changing field. This causes the instantaneous superheating previously described. The temperature of the substance also affects ionic conduction: as the temperature increase, the transfer of energy becomes more efficient.

In a typical reaction coordinate (Figure 1.9), the process begins with reactants (A and B), which have a certain energy level (E_R). In order to complete the transformation, these reactant must collide in the correct geometrical orientation to become activated to a higher-level transition state (E_{TS} - E_R = E_a). The activation energy is the energy that the system must absorb from its environment in order to react. Once enough energy is absorbed, the reactant quickly reacts and returns to a lower energy state (E_p) – the products of the reaction (A-B). Microwave irradiation does not affect the activation energy, but provides the momentum to overcome this barrier and complete the reaction more quickly than conventional heating method.

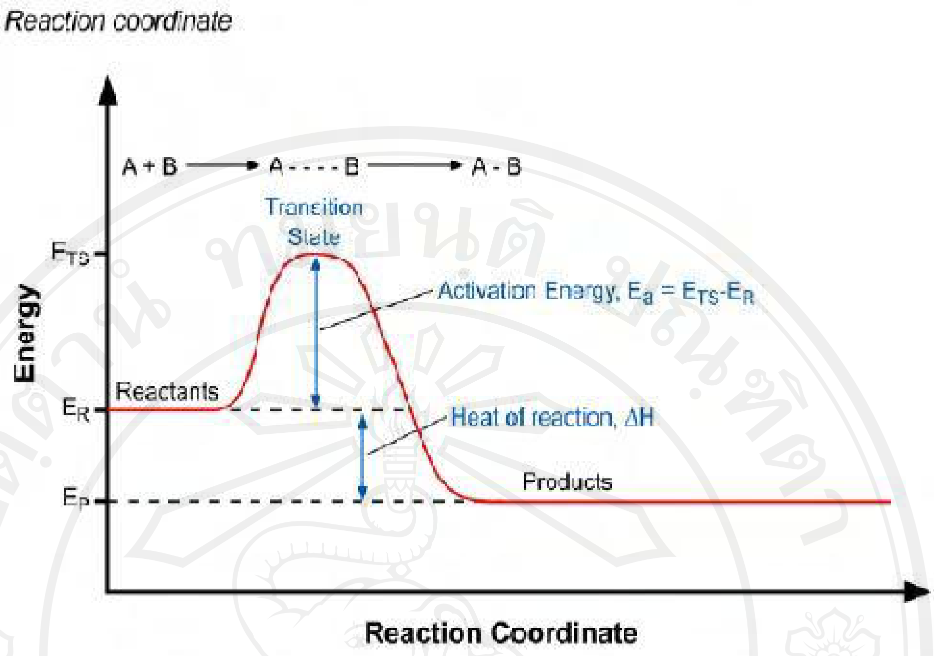


Figure 1.9 Reaction Coordinate.

1.4.3 Fundamental of Microwave Synthesis

The fundamental mechanism of microwave heating involves agitation of polar molecules or ions that oscillate under the effect of an oscillating electric or magnetic field. In the presence of an oscillating field, particles try to orient themselves or be in phase with the field. However, the motion of these particles is restricted by resisting forces (inter-particle interaction and electric resistance), which restrict the motion of particles and generate random motion, producing heat. Since the response of various materials to microwave radiation is diverse, not all materials are amenable to microwave heating. Based on their response to microwaves, materials can be broadly classified as follows:

- Materials that are transparent to microwaves, e.g., sulphur
- Materials that reflect microwaves, e.g., copper
- Materials that absorb microwaves, e.g., water

Only materials that absorb microwave radiation are relevant to microwave chemistry. These materials can be categorized according to the three main mechanisms of heating (Figure 1.10), namely:

- Dipolar polarization
- Conduction mechanism
- Interfacial polarization

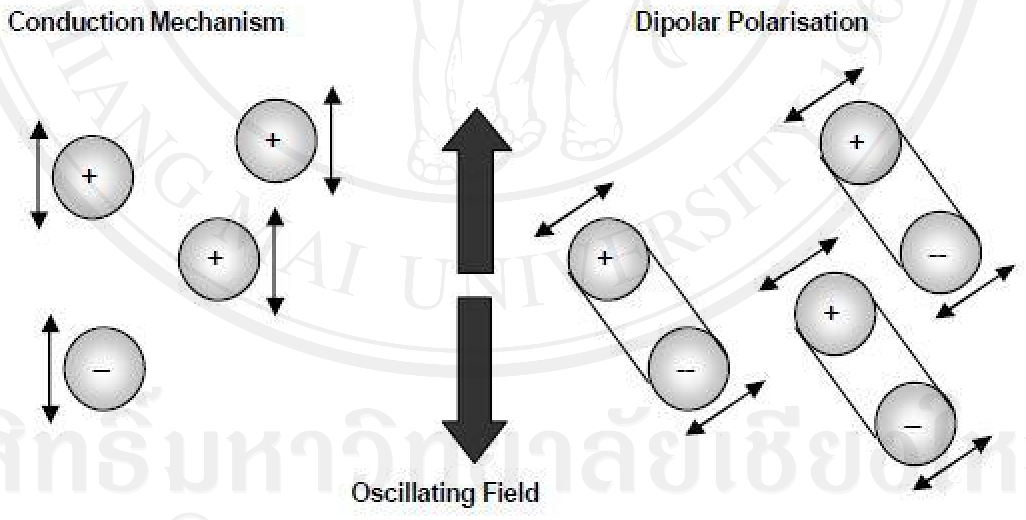


Figure 1.10 Methods of Heating by Microwave Radiation [15].

1. Dipolar Polarization : Dipolar polarization is a process by which heat is generated in polar molecules. On exposure to an oscillating electromagnetic field of appropriate frequency, polar molecules try to follow the field and align themselves in phase with the field. However, owing to inter-molecular forces, polar molecules experience inertia and are unable to follow the field. This results in the random motion of particles, and this random interaction generates heat. Dipolar polarization can generate heat by either one or both of the following mechanisms:

- Interaction between polar solvent molecules such as water, methanol and ethanol
- Interaction between polar solute molecules such as ammonia and formic acid

The key requirement for dipolar polarization is that the frequency range of the oscillating field should be appropriate to enable adequate inter-particle interaction. If the frequency range is very high, inter-molecular forces will stop the motion of a polar molecule before it tries to follow the field, resulting in inadequate inter-particle interaction. On the other hand, if the frequency range is low, the polar molecule gets sufficient time to align itself in phase with the field. Hence, no random interaction takes place between the adjoining particles. Microwave radiation has the appropriate frequency (0.3-30 GHz) to oscillate polar particles and enable enough inter-particle interaction. This makes it an ideal choice for heating polar solutions. In addition, the energy in a microwave photon (0.037 kcal/mol) is very low, relative to the typical energy required to break a molecular bond (80-120 kcal/mol). Therefore, microwave excitation of molecules does not affect the structure of an organic molecule, and the interaction is purely kinetic.

2. Conduction Mechanism : The conduction mechanism generates heat through resistance to an electric current. The oscillating electromagnetic field generates an oscillation of electrons or ions in a conductor, resulting in an electric current. This current faces internal resistance, which heats the conductor. The main limitation of this method is that it is not applicable for materials that have high conductivity, since such materials reflect most of the energy that falls on them.

3. Interfacial Polarization : The interfacial polarization method can be considered as a combination of the conduction and dipolar polarization mechanisms. It is important for heating systems that comprise a conducting material dispersed in a non-conducting material. For example, consider the dispersion of metal particles in sulphur. Sulphur does not respond to microwaves, and metals reflect most of the microwave energy they are exposed to, but combining the two makes them a good microwave-absorbing material. However, for this to take place, metals have to be used in powder form. This is because, unlike a metal surface, metal powder is a good absorber of microwave radiation. It absorbs radiation and is heated by a mechanism that is similar to dipolar polarization. The environment of the metal powder acts as a solvent for polar molecules and restricts the motion of ions by forces that are equivalent to inter-particle interactions in polar solvents. These restricting forces, under the effect of an oscillating field, induce a phase lag in the motion of ions. The phase lag generates a random motion of ions and results in the heating of the system.

1.4.4 Benefits of Microwave Chemistry [15]

Microwave radiation has proved to be a highly effective heating source in chemical reactions. Microwaves can accelerate the reaction rate, provide better yields and uniform and selective heating, achieve greater reproducibility of reactions, and help in developing cleaner and greener synthetic routes.

1. **Increased Rate of Reactions** : Compared to conventional heating, microwave heating enhances the rate of certain chemical reactions by 10 to 1,000 times. This is due to its ability to substantially increase the temperature of a reaction, for instance, synthesis of fluoresce, which usually takes about 10 hours by conventional heating methods, can be conducted in only 35 minutes by means of microwave heating (Table 1.2). At present, there are two main theories that seek to explain the rate acceleration caused by microwaves.

Table 1.2 Comparison of Reaction Duration (in minutes).

REACTION	CONVENTIONAL	MICROWAVE
Synthesis of fluorescence	600	35
Condensation of benzene with urea	60	8
Biginelli reaction	360	35

2. Efficient Source of Heating : Heating by means of microwave radiation is a highly efficient process and results in significant energy saving. This is primarily because microwaves heat up just the sample and not the apparatus, and therefore energy consumption is less. A typical example is the use of microwave radiation in the ashing process. As microwave ashing systems can reach temperatures of over 800 °C in 50 minutes, they eliminate the lengthy heating-up periods associated with conventional electrical resistance furnaces. This significantly lowers average energy costs.

3. Higher Yields : In certain chemical reactions, microwave radiation produces higher yields compared to conventional heating methods, for example, microwave synthesis of fluorescence results in an increase in the yield of the reaction, from 70% to 82% (Table 1.3).

Table 1.3 Comparison of Yields (%).

REACTION	CONVENTIONAL	MICROWAVE
Synthesis of fluorescence	70	82
Condensation of benzene with urea	70	73
Biginelli reaction	70	75
Synthesis of aspirin	85	92

4. Uniform Heating : Microwave radiation, unlike conventional heating methods, provides uniform heating throughout a reaction mixture (Figure 1.11).

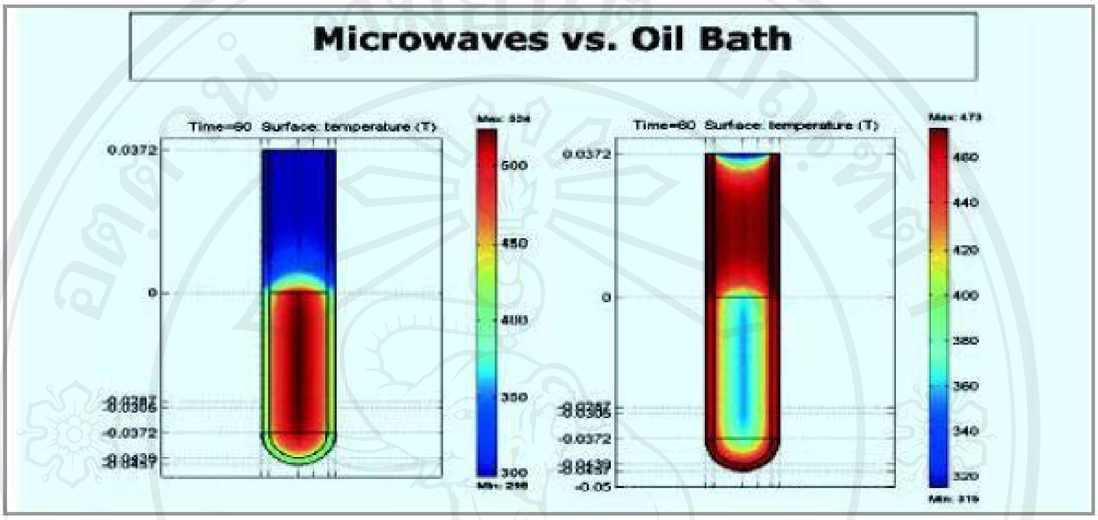


Figure 1.11 Uniform Heating through Microwave Irradiation.

In conventional heating, the walls of the oil bath get heated first, and then the solvent. As a result of this distributed heating in an oil bath, there is always a temperature difference between the walls and the solvent. In the case of microwave heating, only the solvent and the solute particles are excited, which results in uniform heating of the solvent. This feature allows the chemist to place reaction vessels at any location in the cavity of a microwave oven. It also proves vital in processing multiple reactions simultaneously, or in scaling up reactions that require identical heating conditions.

5. Selective Heating : Selective heating is based on the principle that different materials respond differently to microwaves. Some materials are transparent whereas others absorb microwaves. Therefore, microwaves can be used to heat a combination of such materials, for example, the production of metal sulphide with conventional heating requires for weeks because of the volatility of sulphur vapors. Rapid heating of sulphur in a closed tube results in the generation of sulphur fumes, which can cause an explosion. However, in microwave heating, since sulphur is transparent to microwaves, only the metal gets heated. Therefore, reaction can be carried out at a much faster rate, with rapid heating, without the threat of an explosion.

6. Environmentally-friendly Chemistry : Reactions conducted through microwaves are cleaner and more environmentally friendly than conventional heating methods. Microwaves heat the compounds directly; therefore, usage of solvents in the chemical reaction can be reduced or eliminated, for example, Hamelin developed an approach to carry out a solvent-free chemical reaction on a sponge-like material with the help of microwave heating. The reaction is conducted by heating a spongy material such as alumina. The chemical reactants are adsorbed to alumina, and on exposure to microwaves, react at a faster rate than conventional heating. The use of microwaves has also reduced the amount of purification required for the end products of chemical reactions involving toxic reagents.

7. Greater Reproducibility of Chemical Reactions : Reactions with microwave heating are more reproducible compared to conventional heating because of uniform heating and better control of process parameters. The temperature of chemical reactions can also be easily monitored. This is of particular relevance in the lead optimization phase of the drug development process in pharmaceutical companies.

1.5 Hydrothermal / Solvothermal method [18-20]

Hydrothermal/Solvothermal synthesis refers to the synthesis by chemical reactions of substances in a sealed heated solution above ambient temperature and pressure. The reaction can be carried out in water or in any other solvent. When water is used as a solvent, the process is called "hydrothermal process" and when non-aqueous / organic solvents such as methanol, ethanol, polyol, etc. are used, the process is termed "solvothermal process".

They involve the preparation of new materials, the understanding of mechanisms of hydrothermal/solvothermal reactions, and the development of novel synthetic methods and techniques. Understanding the mechanism of hydrothermal/solvothermal reactions is particularly necessary for both the suitable application of a method to a specific synthesis and the exploration of new materials with desired properties.

Basically, the mechanism of hydrothermal/solvothermal reactions follows a liquid nucleation model. It is different from that of solid-state reactions, where the reaction mechanism involves mainly diffusion of atoms or ions at the interface between reactants. However, in the supercritical region of solvent, less data are available at present, and only those for pure water and simple saltwater solutions are known. New methods and strategies play an important role in the investigation of hydrothermal/solvothermal synthesis. The various methods such as induced growth through crystal seeds, structure-directing agent technique, mineralizing, templating, complexing, high temperature and pressure technique, and redox environment control make hydrothermal/solvothermal reactions particularly available for new advanced solid materials.

Figure 1.12 Autoclave for used in Hydrothermal/Solvothermal method [20].

1.6 Literature review

In recent years, microwave radiation method was used to synthesize nanomaterials, as shown below.

In 2004, Verma *et al.* [21] synthesized magnesium ferrite ($MgFe_2O_4$) nanosizes by microwave hydrothermal (MH) method. The average particle size from Gaussian fitting of the as-synthesized $MgFe_2O_4$ is 2 nm. The magnetization of the products at different temperature was investigated, and found that the products exhibited superparamagnetic behavior at 38 K.

Xu *et al.* [22] reported the rapid synthesis of size-controllable YVO_4 nanoparticles by microwave irradiation method without the use of surfactant or template and studied the effect of pH value on the size of the products. The TEM images showed the particle size of YVO_4 powder ranging from 5 to 18 nm. It was found that the products were very sensitive to the pH value. The optical properties of the products were analyzed by UV-Vis spectroscopy, of which the spectra of the YVO_4 showed the highest intensity at the pH of 7.

In 2008, Parhi and Manivannan [23] reported the synthesis and characterization of lanthanide phosphate and vanadate, $LnMO_4$ (Ln = Y and La and M = V and P) by solid-state microwave synthesis at 1100 W for 10 min. The influences of phosphate and vanadate precursors on the formation of $LnMO_4$ (Ln = Y and La, M = V and P) were also investigated.

Park *et al.* [24] reported a self consistently completed solid-state reaction for the synthesis of YVO_4: Eu^{3+}, Sm^{3+} red phosphors using microwave heating, and studied the effect of the Eu^{3+} concentration and co-doping (Eu^{3+} and Sm^{3+}) on the YVO_4 emission, as compared with those by using the conventional furnace heating. XRD technique showed that the co-doping Eu^{3+} and Sm^{3+} increased lattice parameters of the products. When increased Eu^{3+} concentration, the intensities of excitation and red emission spectra were continuously increased until at Eu^{3+} concentration of 3 mol%. Comparing to the conventional furnace heating, the as-synthesized products have the same phase and morphology.

Ma *et al.* [25] synthesized $LaPO_4$:Re (Re = Ce^{3+}, Eu^{3+}, Tb^{3+}) nanorods by refluxing microwave heating method at 60% of the maximum microwave power for 20 min. The $LaPO_4$:Re (Re = Ce^{3+}, Eu^{3+}, Tb^{3+}) nanorods have diameters of 6-30 nm and lengths up to 400 nm.

However, there are many reports on the synthesis of lanthanide metal phosphate compounds by many methods, as shown below.

In 2003, Ruigang *et al.* [26] reported the synthesis of $LaPO_4$ powders by direct solid-liquid reaction of lanthanum oxide and phosphoric acid in water bath. The effect of calcination temperature on phase purity of the products was studied in this research. They found that suitable calcination temperature for producing high purity $LaPO_4$ ceramic is 1,000 ^{o}C. At this calcination temperature, the as-synthesized $LaPO_4$ ceramic has the excellent mechanical property such as high hardness, multiple dislocations and dislocation networks.

Yu *et al.* [27] showed the synthesis of $LaPO_4$ nanowires by hydrothermal method and improved the green emission of $LaPO_4$ nanowires by adding Ce^{3+} and Tb^{3+} as co-activation. The $LaPO_4$ nanowires have the diameter and length of 10-20 nm and 0.5 μm, respectively. The electronic transition rates of Ce^{3+} and Tb^{3+}: $LaPO_4$ nanowires have a little change, comparing to microrods. The energy transfer rate and efficiency of Ce^{3+} to Tb^{3+} in nanowires were reduced.

In 2006, Wang and Gao [28] prepared lanthanum orthophosphate nanorods by solution mixing method in oil bath, and studied the effect of doping Eu^{3+} and Ce^{3+} on photoluminescence property, including discussing the charged transition in the products.

In 2007, Karpowisch *et al.* [29] synthesized and characterized the $CePO_4$ nanoparticles. The XRD showed the transformation from hexagonal to the monoclinic phase after calcination at 800 °C for 8 h. The morphology of $CePO_4$ was investigated by TEM which revealed that hexagonal $CePO_4$ needle-shape changed to monoclinic $CePO_4$ nanoparticles. Moreover, the energy-dispersive spectroscopy (EDS) was used to measure the composition of $CePO_4$ and ^{31}P-NMR was used to study a qualitative of the amorphous phase.

In 2008, Yin *et al.* [30] reported the synthesis and characterization of $CePO_4$ nanowires with a diameter of about 25 nm and length up to several tens of micrometers via water-in-oil microemulsion at room temperature using cerium chloride, sodium orthophosphate, sodium chloride, cyclohexane, Triton X-100 and cetyltrimethyl ammonium bromide as starting materials, and studied the effect of additive and surfactant on the morphologies of the products. The growth mechanism of the $CePO_4$ nanowires was also discussed.

In 2009, Qian *et al.* [31] synthesized light rare earth phosphate ($LnPO_4 \cdot nH_2O$, Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) nanowires via a simple wet-chemical method without adding any surfactants at room temperature. The diameter and length of the as-synthesized rare earth phosphate compounds depend on the lanthanide metal. Moreover, the optical property of doping lanthanide metal in $LaPO_4$ was influenced by pH value and reaction time.

Bao *et al.* [8] prepared and controlled the morphology and size of $CePO_4$ nanostructures by a low temperature hydrothermal at 100 ^oC for 6 h. The products have two phases, the hexagonal and monoclinic. The morphology and size of the products can be controlled by molar ratios of PO_4^{3-}/Ce^{3+} and reaction time. Pure phase of monoclinic $CePO_4$ phase was produced at high molar ratios of precursors. When excessive PO_4^{3-} was added, morphology of the products transformed from rod-like nanoparticles to bundle-like nanorods and flower-like nanostructures, respectively. Finally, the luminescence property of $CePO_4$ nanostructures depended on the phase and morphology of these products.

Schatzmann *et al.* [32] synthesized $LaPO_4$ nanostructure by direct precipitation between $La(NO_3)_3 \cdot 6H_2O$ (solid and solution) and hot phosphoric acid. The products showed two morphologies, which depend on the state of $La(NO_3)_3 \cdot 6H_2O$ adding into the hot phosphoric acid. Rice-like (200-400 nm) and flower-like (5-10 μm) $LaPO_4$ shapes were obtained by adding solid and solution of $La(NO_3)_3 \cdot 6H_2O$.

Yu *et al*. [33] prepared $LnPO_4$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho) nanoparticles by a facile ultrasonic irradiation method without adding a surfactant. The as-synthesized $LnPO_4$ has two different types of crystal structure, the hexagonal and tetragonal, identified by XRD analysis. They claimed that the possible growth mechanism of hexagonal $LnPO_4$ nanorod bundles, caused by the short collapse between a few nuclei in the collapsing bubbles, and concluded that ultrasonic irradiation assisted controlling the particle growth of nanorod bundles.

In 2010, Guan *et al*. [34] prepared $CePO_4$ nanofibers by solid-solution method using $Ce_2(CO_3)_3$ and $H_6P_4O_6$ as raw materials in an autoclave at 100 ^{o}C for 12 h. Only nanofibers were obtained when the concentration of $H_6P_4O_6$ was increased. TEM image shows $CePO_4$ nanofibers with the diameters of 20-50 nm and length up to several tens of micrometers.

1.7 Research Objectives

1.7.1 To develop the synthesis method for $LnPO_4$ (Ln = La and Ce) materials using microwave irradiation.

1.7.2 To investigate and characterize the phase, morphology, atomic vibration, and optical properties of $LnPO_4$ (Ln = La, Ce) by XRD, SEM, TEM, FTIR, UV- vis and PL spectrometry.