

Chapter I

General Introduction

In recent years, crystals have been the subject of intense research stemmed from their tremendous applications in various industries like electronic, photonic and fiber optic communications, *etc.* The crystals can also be used as semiconductors, superconductors, transducers, polarizers, radiation detectors, magnetic garnets, ultrasonic amplifiers, non-linear optics, solid state lasers, piezo-electric, photosensitive, electro-optic and acousto-optic devices.¹⁻⁵ Fig 1.1 gives us a picture of increasing demand and growing interest in the design and development of crystals.⁶ Crystal growth, being an interdisciplinary subject, covers physics, chemical engineering, material science, mineralogy, metallurgy, crystallography, *etc.* However, it is always difficult to synthesize good quality dislocation free single crystals than poly-crystalline material; thus an extra effort is required in preparing single crystals having outstanding applications in various industries.

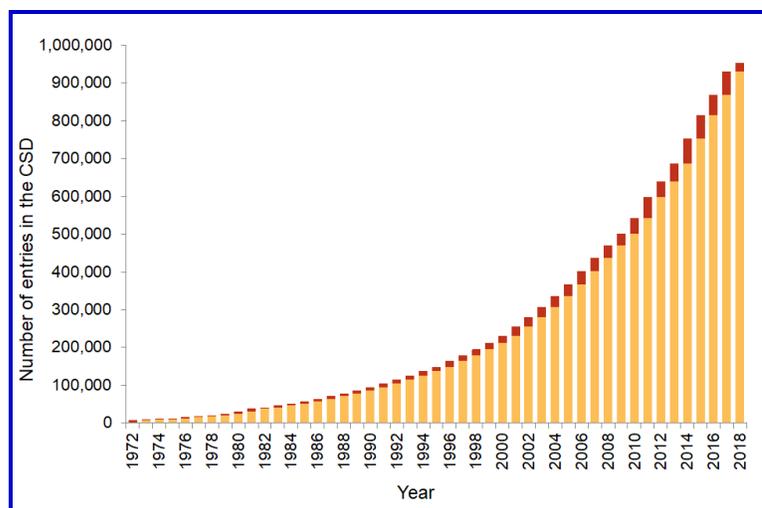


Fig 1.1. Year wise entries of crystals to the Cambridge Crystallographic Data Centre.

The physical properties of the solids are obscured and complicated due to the presence of grain boundaries. But pure single crystals are anisotropic having uniform composition and absence of grain boundaries between the grains, thereby eliminating the complications in physical properties. In order to achieve better performance from

the molecular devices, good quality dislocation free single crystals are required and thus the growth of single crystals and their use towards device fabrication have gained tremendous impetus for both in academic and applied research.

1.1. Single crystals

The periodic atomic, molecular/ionic arrays, with repeated distances are known as single crystals. In single crystals, the crystal lattice of the entire sample is continuous with unbroken edges and no grain boundaries.⁷

1.2. Crystal systems

A crystal system is a set of point groups wherein the point groups and their corresponding space groups are assigned to a lattice system.⁸ There are 32 point groups in three dimensions and most of them belong to only one lattice system. In such cases, both the lattice system and crystal system have same name. There are five point groups assigned to rhombohedral and hexagonal lattice systems exhibiting three-fold rotational symmetry and thus are assigned to trigonal crystal system.

1.3. Bravais lattices

Bravais lattices, referred to as space lattices, describe the geometric arrangements of the lattice points and translational symmetry of the crystals. In three dimensions, there are 14 Bravais lattices⁹⁻¹² that describe the translational symmetry. All recognized crystalline materials, except quasi-crystals, are assigned these descriptions. The designations are primitive (*P*), body-centered (*I*), face-centered (*F*), face-centered in one of the faces (*C*) and rhombohedral (*R*). For example, a monoclinic structure with space group $P2_1/c$ belongs to primitive Bravais lattice.

1.4. Thermodynamic Aspects of Crystallization

The fundamental condition for crystallization of a stable solid phase from a metastable fluid (starting) phase is due to deviation from thermodynamic equilibrium. Fig 1.2 depicts the free energy (*G*) versus temperature (*T*), of two phases in contact with each other in the neighborhood of first-order phase transition. Their difference, *i.e.*, $\Delta G = G_f - G_s$ is the driving force or growth affinity of crystallization. This free energy change (ΔG) can be related to super cooled melts, supersaturated vapors and supersaturated solutions. These relations are briefly described below:

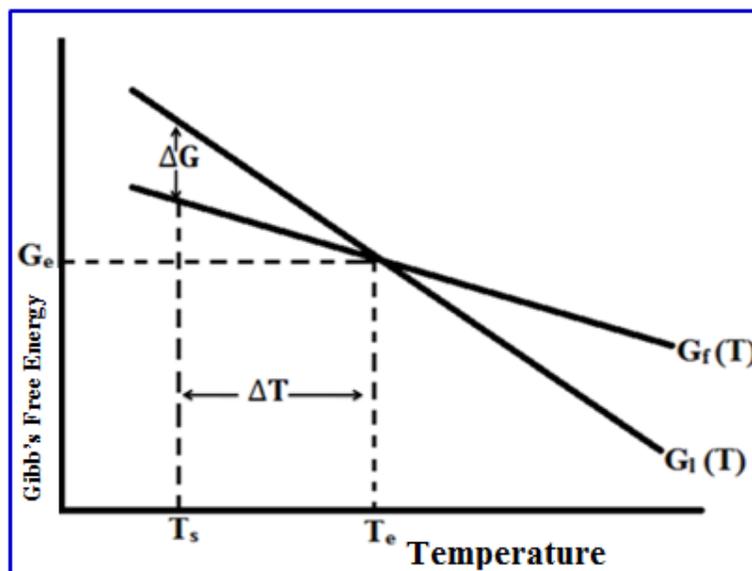


Fig 1.2. Dependence of the free energies (G_f and G_s) on the temperature (T).

a) **Supercooled Melt:** The free energy change for a supercooled melt for the temperature difference (ΔT) can be written as,

$$\Delta G = \Delta H \frac{\Delta T}{T} \quad (1)$$

where ΔH is the enthalpy released when 1 mol of solid crystallizes and T_e is the melting point. When ΔT is large or ΔH is small, then ΔH in Eq (1) can be corrected to allow for the difference in specific heats of the solid and the liquid. This results in the inclusion of an additional term ΔT^2 .¹³ Values of ΔT rarely exceeds 10 K. Values of $\Delta H / T_e$ usually falls between 10 to 100 $\text{JK}^{-1}\text{mol}^{-1}$ and values of ΔT are typically 1K, thus ΔG becomes 100 J/mol, and $\Delta G < RT$.

b) **Supersaturated Solutions:** The free energy change for a supersaturated solution can be written as,

$$\Delta G = nRT \ln \left(1 + \frac{\Delta c}{c_e} \right) \approx nRt \frac{\Delta c}{c_e} \quad (2)$$

where n is number of ions formed by one molecule of the solute in solution, R is the universal gas constant, T is the absolute temperature and Δc is the concentration of

solute exceeding the equilibrium concentration (c_e). The relative supersaturation can be expressed as:

$$\sigma = \Delta c / c_e \quad (3)$$

The values of σ are basically less than 0.1. If ΔH is the enthalpy of solution, Eq (1) is used to describe the growth of crystals from a solution cooled below its saturation temperature. The supercooling was ascertained for the growth of single crystals of quartz under hydrothermal conditions.¹⁴

c) Supersaturated Vapour: The free energy change for a supersaturated vapor can be written as,

$$\Delta G = nRT \ln \left(1 + \frac{\Delta P}{P_e} \right) \approx nRt \frac{\Delta P}{P_e} \quad (4)$$

where $\Delta P = P - P_e$, P is actual partial pressure and P_e is equilibrium pressure of the vapours. If ΔH is considered as the enthalpy of vaporization, then Eq (1) expresses ΔG in terms of cooling of the vapor from its equilibrium temperature. The value of $\Delta P / P_e < 0.1$ and ΔG is approximately 1 kJ/mol. In the simplest possible free energy–spatial position model of a crystal–fluid interface (Fig 1.3), an energy barrier G_1 separates the crystal from the fluid. Therefore, the transfer rate from the fluid to the crystal should be proportional to $e^{-G_1/RT}$ and the rate from crystal to fluid should be proportional to $e^{-(G_1+\Delta G)/RT}$. Thus, the net rate of transfer to the crystal should depend on $e^{-G_1/RT}(1 - e^{\Delta G/RT})$, which for $\Delta G RT$ reduces to $\Delta G e^{-(G_1/RT)/RT}$. It is always very difficult to determine the exact value of G_1 . This denotes that the activation energy for volume diffusion in the fluid phase, *i.e.*, viscous flow in the melt (of the order of 5–50 kJ mol⁻¹).¹⁵ At the interface of crystal–solution, solvation shells form/disintegrate and requires higher activation energies (desolvation or dehydration energy), yielding G_1 in aqueous solutions of 50–100 kJ mol⁻¹.¹⁴

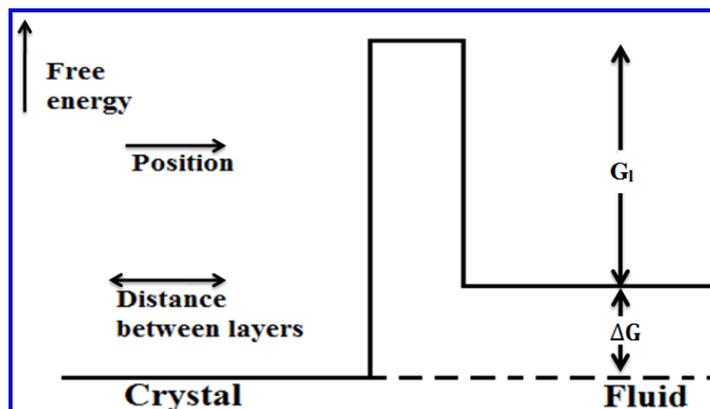


Fig 1.3. Free energy as a function of simple model of crystal–fluid interface.

1.5. Methods of crystal growth

Crystal growth is an art rather than a science. Presently, chemists involved in crystal growth have moved from the periphery to the core of material-based technology. The various methods used for crystal growth to obtain good quality crystals are discussed in this chapter. The growth aspects differ from crystal to crystal depending on the physical and chemical properties like melting point, solubility, phase change, decomposition, *etc.* Different crystal growth techniques²³ are listed in Table 1.1 and these techniques were discussed briefly herein this chapter.

Table 1.1. Different crystal growth techniques.

Types	Techniques
Melt growth	a. Bridgman method b. Czochralski method c. Kyropoulous method d. Verneuil method e. Zone melting method f. Strain annealing method
Vapour growth	a. Chemical transport method b. Physical transport method
Solution growth	a. Low temperature solution method b. High temperature solution method c. Hydrothermal method d. Gel method

1.5.1. Crystal growth from melt

1.5.1.1. Bridgman method

The materials with volatile constituents can be used for the growth of single crystals using this method. In this method,^{14, 23} the material used for the growth of crystals was taken in a cylindrical container and melted. The container was then tapered conically with a point bottom. The temperature of cylindrical container is lowered slowly from the hot zone of the furnace in to the cold zone.

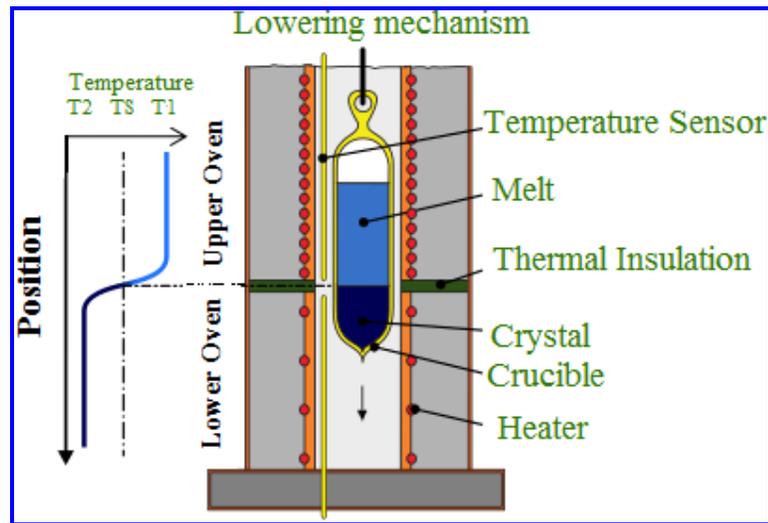


Fig 1.4. Schematic representation of Bridgman method.

Crystallization begins at the tip and continues to grow from the first formed nucleus. The latent heat of solidification is released through the crucible and the crystal. This method is technically simple and can produce crystals of reassigned diameter. Fig 1.4 shows the schematic diagram of Bridgman experimental setup.

1.5.1.2. Czochralski method

The Czochralski^{15,23} technique can be used to obtain large and dislocation free crystals in very short time. The technique is shown schematically in Fig 1.5. In this method, the material to be grown is melted by induction heating under controlled conditions in a non-reacting container. A seed crystal is fixed to a rod in a desired orientation. The seed is lowered into the molten material whose temperature is adjusted to allow atoms to attach to the seed at a rate determined by the temperature and the cooling effect of the rod and the seed. At first the seed is slightly melted and

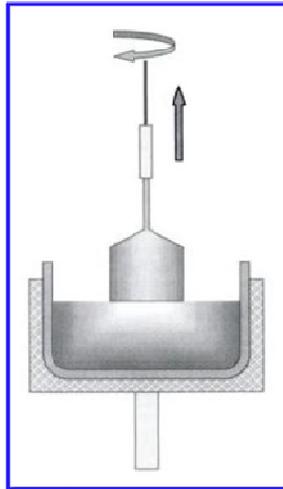


Fig 1.5. Schematic representation of Czochralski method.

then pulled carefully with simultaneous rotation of the seed rod and crucible to grow unstressed single crystals. This method has a number of advantages as stress free single crystals can be grown and crystal growth kinetics can also be studied at any stage. This method has gained popularity in growing single crystals of germanium, silicon, gallium arsenide and gallium phosphide, *etc.*

1.5.1.3. Kyropoulos method

In Kyropoulos^{14, 24} technique, the crystals with larger diameter can be grown. In this method the seed is brought in contact with the melt and raised little bit during the growth so that only a part of the seed melts and a short narrow neck is grown. Then the vertical motion of the seed is stopped and growth initiated with decreasing the power of the melt. The alkali metal halides for optical components can be grown using this technique.

1.5.1.4. Vernuil method

This method is a commercial method^{17, 24} of growing crystals of high melting point. The powdered material is shaken electrically or mechanically from a hopper through the sieve, using a vibrator of low amplitude capacity. The oxy-acetylene or oxyhydrogen flame is allowed to impinge on a pedestal where a small pile of partly fused alumina quickly builds up. As the pile rises, it moves into the hotter part of the flame and the tip gets completely molten. The molten region first increases in size and

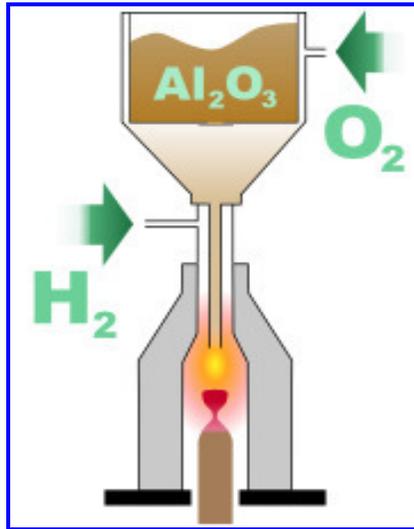


Fig 1.6. Schematic representation of Vernuil apparatus.

then starts to solidify at the lower end. As the movement of powdered materials increases, the solidifying region broadens into a crystal growing in length. Such a crystal is called boule. The method has been schematically illustrated in Fig 1.6. It is technically simple and the growth kinetics of crystals can be observed. Single Crystals of various shapes like hemi-spheres, plates, discs and cones can be grown by this method. Oxide crystals can also be grown by regulating the H_2/O_2 ratio in the flame. A major demerit of this method is that the growing crystals are exposed to a steep temperature gradient.

1.5.1.5. Zone melting method

This technique^{18, 22} is mainly used for purification of semiconductors. This technique is illustrated in Fig 1.7. The material to be crystallized is in the form of free standing rod clamped at one of its end and a small zone of it will be melted by moving induction heater. The melt is suspended in the form of drop between the two parts of the rod and thus named as float zone melting. This molten zone is then moved through the rod over its whole length by the motion of heater. A single crystal can be generated as a result of spontaneous nucleation.

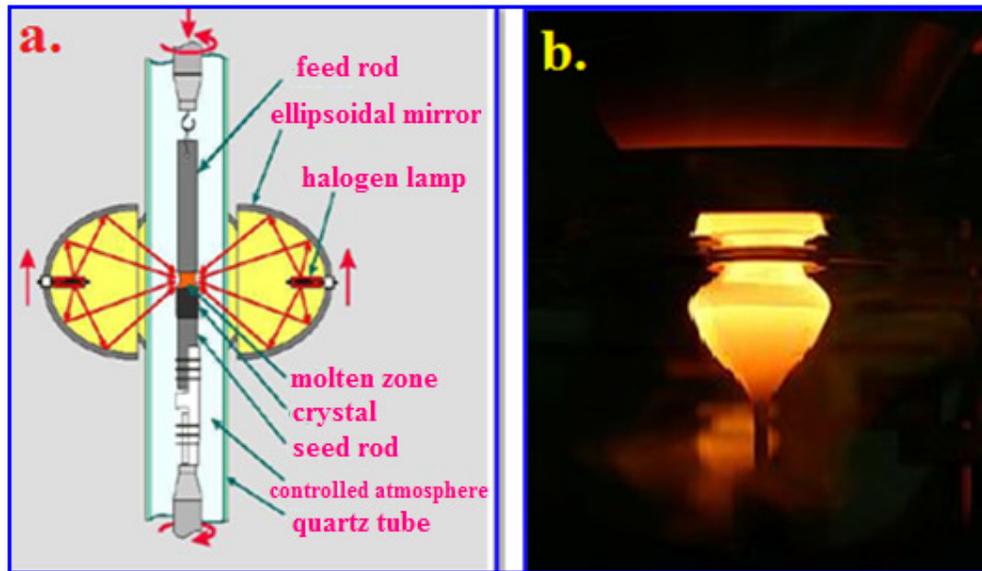


Fig 1.7. (a) Schematic diagram of Zone melting furnace and (b) Silicon crystal at the beginning of growth process.

1.5.1.6. Strain-Annealing method

In this method,^{19,23} the metal rod in the form of fine grain structure is subjected to strain at increased temperature. Working and annealing at low temperature produce a fine grain structure. In materials having solid-state transitions, the strain induced by changing the phase can be used to device crystallization and the specimen is annealed alternatively below and above the transition temperature.

1.5.2. Growth from vapour

Vapour growth²⁴ techniques were used to grow the crystals that are sublimable under ambient conditions. This method can be used to obtain bulk crystals and epitaxial films. This growth method is very costly in terms of deposition of large volumes of the materials. This method can be classified as Physical and Chemical vapour transport

a) Physical vapour transport:

In this method,²⁴ the crystals are grown from its vapour. The vapour diffuses from hotter end and undergoes condensation at the colder end leading to the formation

of single crystals. This method can be used to obtain bulk crystals. Diamond, silicon and other crystals can be grown using this method.

b) Chemical vapour transport:

In this method²⁴ the source and the transporting agent undergoes chemical reaction forming gaseous products. This product disperses to colder end where reaction is reversed, so that the product decomposes and required crystal is deposited. The transporting agent diffuses to hotter zone to react with other charge.

1.5.3. Growth from solution

In this technique,²³ the chemical components are dissolved in a solvent or flux and then allowed to crystallize slowly with decrease in temperature. In this method crystals can be synthesized from a solution well below its melting point and perhaps even at room temperature. Depending on the solubility of the crystalline materials, this method can be classified as low and high temperature solution growth.

1.5.3.1. High temperature solution growth

This method is applied to materials with incongruent melting point. Mixed crystals of solid solutions can be grown by choosing suitable growth parameters. High temperature solution growth of crystals can be classified as: i) Flux method and ii) Hydrothermal method.

i) Flux method:

It is a high temperature solution growth method²¹⁻²² which is used to grow variety of single crystals like barium titanate, magnesium oxide, *etc.* In this method, the crystals are grown from molten state (known as flux) at high pressure and temperature. The solvent is evaporated and the melt is cooled slowly so that crystallization occurs by spontaneous nucleation. Since the process is carried out in the sealed or partly sealed platinum crucibles, the growth kinetics cannot be measured by this method. The crystals grown are highly transparent and can be used for optical experiments without further polishing. Synthesis of very small crystals is the demerit of this method.

ii) Hydrothermal method:

Hydrothermal method²⁴ is suitable for the growth of materials that are practically insoluble in water. Many metals, metal oxides and other compounds show

a significant solubility when the pressure and temperature are increased. In this method, growth is generally performed in steel autoclaves with silver, gold or Teflon coatings. The rate of growth depends on the temperature difference between top and bottom of the autoclave, pressure and the amount of mineralizers present. The requirement of high pressure cause practical differences. Hence large, high purity, dislocation free single crystals can be grown using this method. Quartz crystals are grown industrially using this technique.

1.5.3.2. Low temperature solution growth

This is one of the ancient methods of growing crystals from solution. The growth of crystals may take long time such as weeks to months and even years. This method²⁵⁻²⁶ is used to grow the single crystals unstable at melting point and also the materials undergoing phase transformations below its melting point. Materials soluble at ambient temperature to 100 °C under atmospheric pressure are grown using this method. The mechanism of growing crystal from solution is governed by the interaction of solvent molecules or ions and the solute, which in turn depends on thermodynamic parameters like pressure, temperature and also on the nature of solvent. This method allows to grow crystals of different morphology and polymorphic for the same materials using different growth conditions and solvents.

The supersaturation can be achieved by employing the following methods:

a) Slow cooling of the solution:

The best way of growing single crystals from solution is the slow cooling of the solution. In this method,²⁴⁻²⁶ growth takes place without secondary nucleation in the solution, provided the supersaturation is attained in the metastable zone. The rate of cooling may lead to change in the solubility beyond this zone and multi-nucleation takes place at the expense of seed crystal. It is mandatory to maintain a temperature balance between lowering of temperature and growth rate. Growth at low supersaturation point prevents strain and dislocation at the interface. Supersaturation may be increased after initial growth to arrive at a reasonable growth rate.

b) Slow evaporation method:

In this method,²⁵⁻²⁶ the excess of solute is established by using the difference between rate of evaporation of solute and the solvent. In this method, the particles of the solution that are loosely bound to the components are lost resulting in decrease of

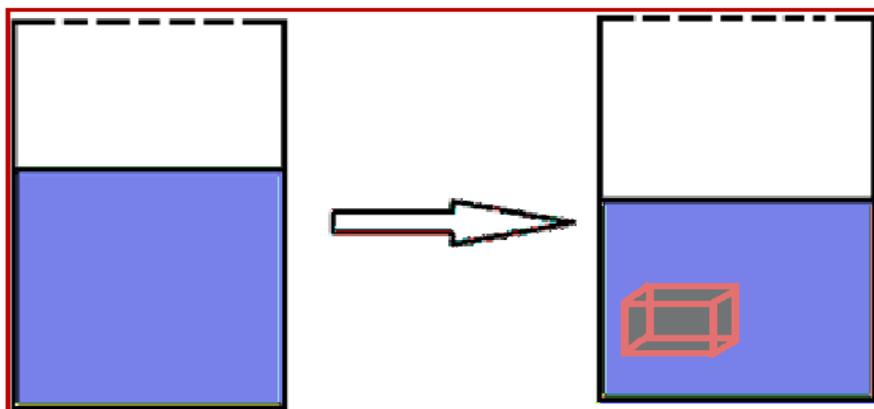


Fig 1.8. Schematic representation of slow evaporation method.

volume of the solution. In most of the cases, the solvent evaporates rapidly resulting in supersaturated solution evaporate. Water being non-toxic is allowed to evaporate and escape freely to the atmosphere. This is one of the simplest and oldest methods of crystal growth. Fig 1.8 shows the schematically represents the slow evaporation method.

c) The temperature gradient method:

In this method,²⁴⁻²⁶ the materials are transported from a hotter region to containing solute to cooler region. This results supersaturation of the solution and the growth of crystals take place. A slight difference in the temperature of source and crystal zones effectively affects the growth rate of crystals. The major advantage of this method is that the Crystal grows at fixed temperature and insensitivity to changes in temperature provided both the source and growing crystal undergo the same change.

d) Gel method:

Gel, a two component semi-solid, is rich in liquid and is inert in nature. The materials undergoing decomposition before melting is grown in gel medium²⁵⁻²⁷ by counter diffusion of two suitable reactants. Crystals of several millimeter dimensions

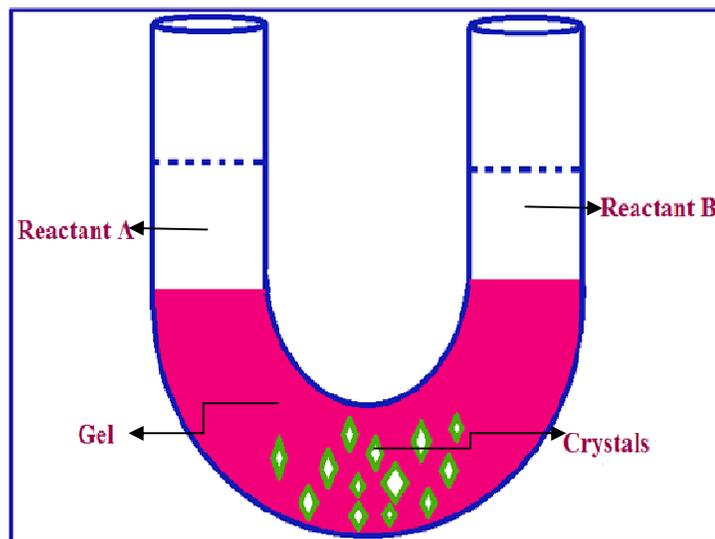


Fig 1.9. Schematic representation of Gel method.

can be grown within 3-4 weeks. This room temperature crystal growth may lead to the formation of good quality with lesser defective crystals. The method has been shown schematically in Fig 1.9.

1.6. Metal-Organic Hybrid Complexes

Metal-organic hybrid networks have been studied intensively over recent decades due to their porosity and fascinating magnetic and electronic properties. These properties lead to their potential applications in gas absorption, gas storage, catalysis and sensors.²⁸⁻²⁹ Common alternate terms for hybrid materials include “coordination polymers”, “metal organic frameworks/networks” and “hybrid networks”. Inorganic-organic hybrid materials in which metal coordination compounds of finite one-, two-, three-dimensional network structures with metal ions as backbones and ligands are called “coordination polymers”.³⁰

Metal-organic frameworks (MOFs)³¹ are defined as extended array of metal ions or complexes linked by multifunctional bridging organic ligands. MOFs are geometrically well-defined three-dimensional networks with strong bonding (such as covalent bonding) within the structure. Metal-organic hybrid networks are crystalline materials containing both organic and inorganic moieties as integral parts of the network with extensive bonding interactions like covalent, ionic or hydrogen bonds

throughout the entire material. The hybrid concept falls into a category where the interface between their components is increased compared to a mixture and the interaction is at a molecular or atomic level. Structure property relationship activity is the key characteristic factor for the functional hybrid materials. Inorganic-organic hybrid compounds can be divided into two categories. First is metal-organic framework (MOF), wherein an organic component is covalently bonded to basically a metal centre and second one is organically templated inorganic materials which have no or very weak interactions (like hydrogen bonding, *etc.*) between inorganic and organic components.

1.6.1. Methods of synthesis of metal-organic hybrid complexes

There are a number of methods employed for the synthesis of metal-organic hybrid complexes that attracted the scientist across the world. Some of the popular methods used for the synthesis of hybrid complexes are discussed below:

1.6.1.1 Conventional method

This method³² involves heating of the mixture containing metal salt and organic linker in a solvent. The complexes thus prepared are filtered and washed properly using suitable solvents. The complexes prepared using conventional methods are often found to be thermally unstable and may even react with the solvents used. This results in the cleavage of bonds as well as formation of metal sites or cavities for guest species like gases to access the pores formed within their structure. Moreover the conventional methods are time consuming.

1.6.1.2. Solvothermal method

Solvothermal synthesis³³⁻³⁴ of metal-organic hybrid complexes is performed in an autoclave in aqueous/non-aqueous precursor solution. In this method, the temperature is usually maintained above critical point of the solvent under high pressure. Solvothermal synthesis allows controlling the size, shape and also the crystalline nature of the hybrid complexes. The characteristic features of the synthesized complexes can be altered by changing the temperature, reaction time, surfactants and precursor type. In this method the organic linkers and the metal salts are heated in aqueous/non-aqueous solvents at high pressure and temperature. The method is schematically represented in Fig 1.10.

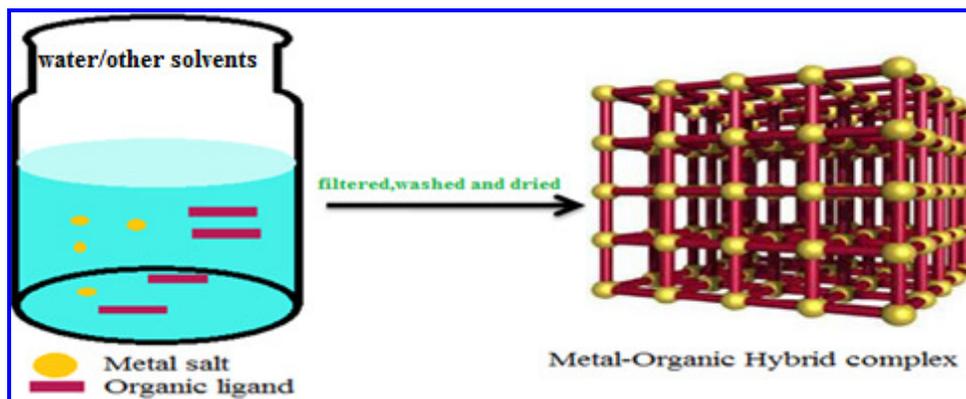


Fig 1.10. Schematic representation of Solvothermal method.

1.6.1.3. Hydrothermal method

In this method, the aqueous suspension of the reaction mixture is loaded in Teflon vessel, sealed and placed in the automated oven/microwave unit. The reaction mixture is heated for the appropriate time at the set temperature. After the reaction is complete, the vessel is left for hours to cool at room temperature.

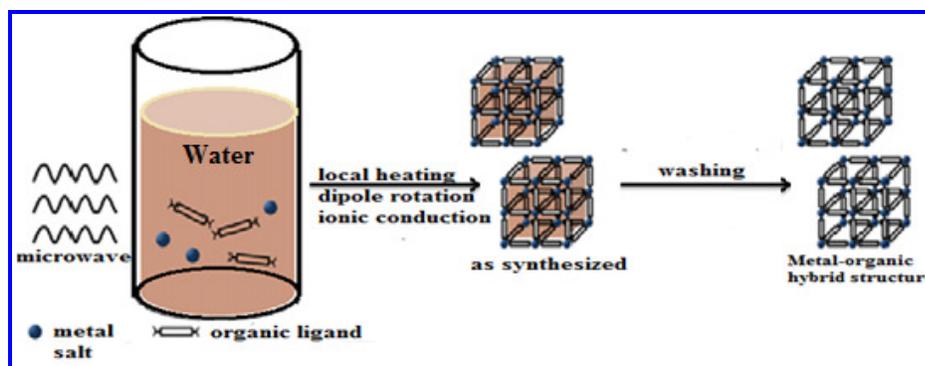


Fig 1.11. Schematic representation of Hydrothermal method.

Then it is filtered and after repeated washing with de-ionised water and other solvents the compound is isolated and used for physicochemical characterization and also the potential applications is explored. The molecular rotations and fast heating of liquid is induced by coupling the oscillating electric field coupled with dipole moment of the molecules present in the medium.³⁵⁻³⁶ The potential applications of this method is faster crystallization, phase selectivity,³⁷⁻³⁸ narrow particle size distribution³⁹ and facile control of morphology.⁴⁰⁻⁴¹ Commercial microwave can also be used to provide adjustable power outputs and enable fiber optic pressure- temperature control.⁴²

1.6.1.4. Sonochemical Method

Sonochemical methods can achieve reduction faster crystallization and significantly smaller particles than those obtained from the conventional solvothermal synthesis.⁴³⁻⁴⁴ As shown in Fig1.12, the reaction mixture for the given metal-organic hybrid complexes is introduced to a Pyrex reactor fitted with a sonicator bar. The power output can be adjusted without external cooling. The formation and collapse of bubbles in the solution after sonication (acoustic cavitations), produces very high temperatures of around 5000 K and pressures of about 1,000 bar.⁴⁵⁻⁴⁶ This results in increased heating and cooling rates thereby producing fine crystallites.⁴⁶ High-quality metal-organic hybrid crystals were obtained within 30 minutes by sonochemical synthesis using 1-methyl-2-pyrrolidone as the solvent.⁴⁷

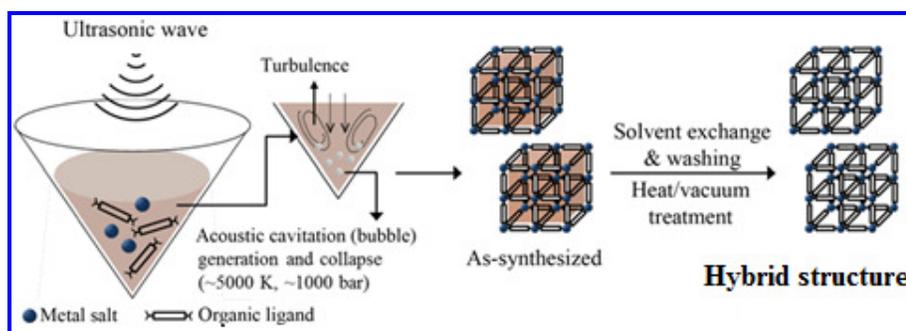


Fig 1.12. Schematic representation of Sonochemical method.

1.6.1.5. Electrochemical Method

In electrochemical synthesis, metal ions are continuously supplied through anodic dissolution. The source metal ions react with the organic linker molecules and also with a conducting salt present in the medium. The deposition of metal on the cathode is avoided using protic solvents.⁴⁸ The electrochemical route can be used to obtain higher solids contents compared to normal batch reactions.⁴⁶

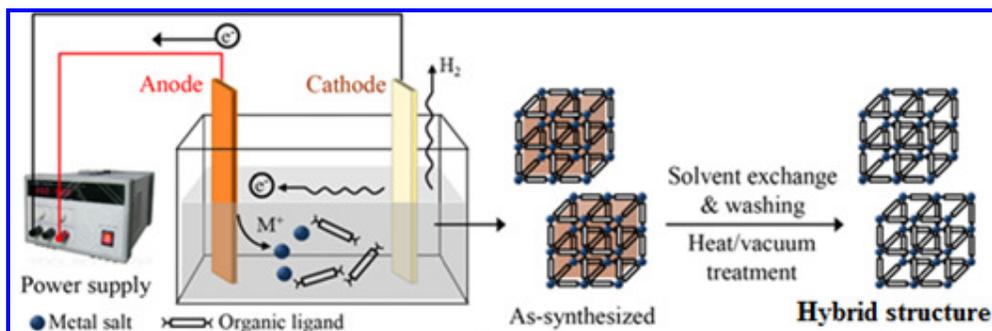


Fig 1.13. Schematic representation of the Electrochemical method.

1.6.1.6. Mechanochemical Method

This method involves intramolecular breakage of bonds followed by chemical transformations in solvent free conditions at room temperature.⁴⁹ Hybrid complexes in good yield can be obtained in very short time, *i.e.*, in 10-60 mins. Metal oxides were often preferred over metal salts as a starting material to obtain water as the only side product.⁴⁶ Kitagawa *et al.* has reported the critical role of moisture in the synthesis of pillared type hybrid complexes using this method.⁵⁰ This method can be enhanced by increasing small amount of solvents which increases rate of mobility of the reactants.⁵¹⁻⁵²

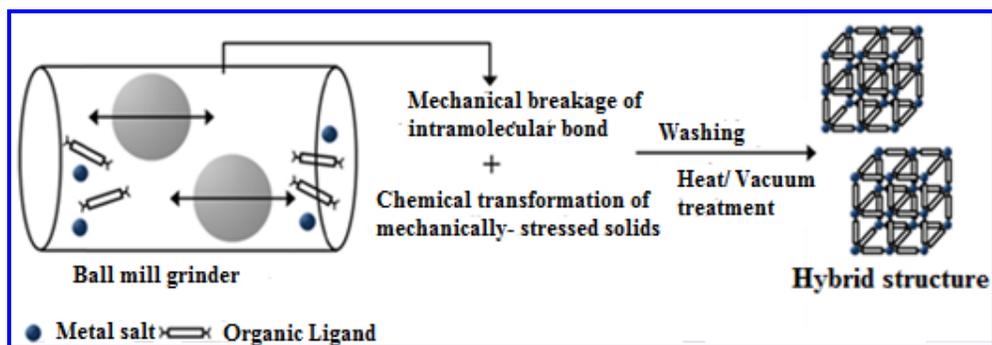


Fig 1.14. Schematic representation of Mechanochemical method.

1.6.2. Applications of metal-organic hybrid complexes

Metal-organic hybrid complexes have shown potential applications in gas adsorption, gas separation, and catalysis.⁵³⁻⁵⁹ In the past few decades, remarkable progress have been observed in the design, synthesis and characterization of hybrid complexes stemmed from their fascinating chemical and structural diversity and also

due to their huge potential applications. The intense research efforts towards the industrial applications are mainly attributed to the unique structural properties like robustness, high chemical and thermal stabilities.

1.6.2.1. Biomedical applications

Metal-organic hybrid complexes are termed as 'hybrid route' for drug delivery due to its flexible skeleton provided by tunable pore volume and functional organic groups. The pore size is tailored to increase storage capacity and release time for specific drug molecules. To consider hybrid complexes as a potential drug carrier, it should have efficient drug loading and drug delivery capacity with controlled release of the drug, and also matrix degradation in the body. MIL-100 and MIL-1013 exhibited a very high drug storage capacity, up to an unprecedented 1.4 g of Ibuprofen per gram of porous solid and have shown efficient as well as controlled drug release under physiological conditions within 3 to 6 days.⁶⁰⁻⁶²

1.6.2.2. Chemical Sensors

The performance and use of chemical sensors are optimized considering the various elements like selectivity, sensitivity, material stability, response time and reusability. MOFs/hybrid with luminescent properties along with shape/size selective sorption properties are considered as good sensing devices.⁶³⁻⁶⁸ The organic linkers/ligands present in the framework show ready luminescence following UV-Vis excitation.⁶⁷ The potential selection of hybrid materials for specific analytes is substantial but not developed enough to adsorb atoms/molecules smaller than the aperture size.⁶⁵ The open metal sites plays crucial role in molecular recognition owing to their ability to impart highly specific and selective molecular transport, transformations and storage.⁶⁹

1.6.2.3 Catalysis

Metal-organic hybrid complexes can be used as potential catalysts stemmed from their tunable porosity with large surface area, diverse coordination geometries, polytopic linkers, ancillary ligands and diversity in metal and functional groups. Moreover, the metal ion in the hybrid complexes often acts as Lewis acids and activates the coordinated organic substrates for subsequent organic transformations like the cyanosilylation of aldehydes as well as imines.⁷⁰

1.6.2.4 Gas Separations

Metal-organic hybrid complexes/MOFs have been found to be used as gas separating materials attributed to their tunable pore size, surface area and other surface properties. Hybrid complexes have diverse coordination geometries and can be used as effective tool in gas separation. The separation of gases from mixture is necessary from environment perspective, *e.g.*, it is necessary to remove CO₂ from CH₄ to avoid environment hazard.⁷¹⁻⁷² The membrane separation technology is used to efficiently and selectively capture CO₂ from the mixture. The interaction between the polymeric membranes and gases are tuned effectively to increase both selectivity and efficiency of gas separations from the stream of gases.

1.6.2.5. Gas Storage

MOFs/hybrid complexes have emerged as new promising family of materials for the storage of gases attributed to their substantial pore volume and flexible geometry. The capture and storage of CO₂ from exhaust flue plays significant role in mitigating its effect on climate change. The elimination of CO₂ for upgrading natural gas or purifications of hydrogen is economically important. MOFs are more compatible and economical than other techniques for storing CO₂.⁷³ MOFs are also considered for storing H₂ gas. Metal centers having high binding energies can bind hydrogen gas directly.¹¹⁷

1.6.3. Water as a reaction medium

Water shows remarkable properties as reaction media under hydrothermal conditions especially at critical point and above 100 °C temperature and above 1 atm pressure. The chief advantages of using water as reaction medium is that it is polar, non-toxic, non-mutagenic, non-flammable, non-carcinogenic and thermodynamically stable. Moreover, it acts as a catalyst in the synthesis of useful compounds by tuning the pressure and temperature. Water being volatile, can be removed easily from the products. The phase diagram of a homogenous substance (Fig 1.15) marks the end for the liquid-vapour coexistence curve at the critical temperature T_c and pressure P_c . A supercritical fluid (SCF)⁷³ is an intermediate phase between a gas and a liquid. The density of both the phases become the same at the critical point and thus known as supercritical fluid (SCF).

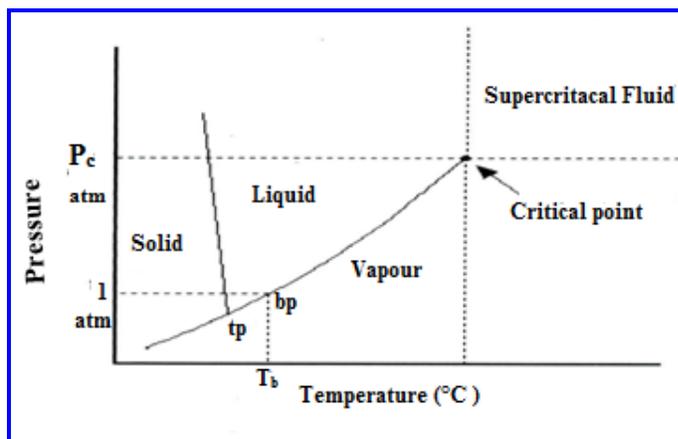


Fig 1.15. Phase diagram of water. Adapted from Ref. No 74.

Viscosity and diffusivity symbolizes transport properties and influences the rate of mass transfer. In SCF diffusivity of reactants will occur faster than in liquid solvents, *i.e.*, solids dissolve and migrate faster in SCFs. Intermediate density, low viscosity and high diffusivity of water increases the rate of the reaction. In the compressible region, the sharp increase of dielectric constant⁷³ with pressure refers to the area close to critical point in which the compressibility is higher than forecasted from ideal gas law. This behavior is parallel to the change of density as shown in Fig 1.16.⁷⁴ Density changes continuously and sharply with increasing pressure in compressible region. The significant change in solvating power of hydrothermal solvents can be observed with change in density. This seems to be advantageous over other solvents.

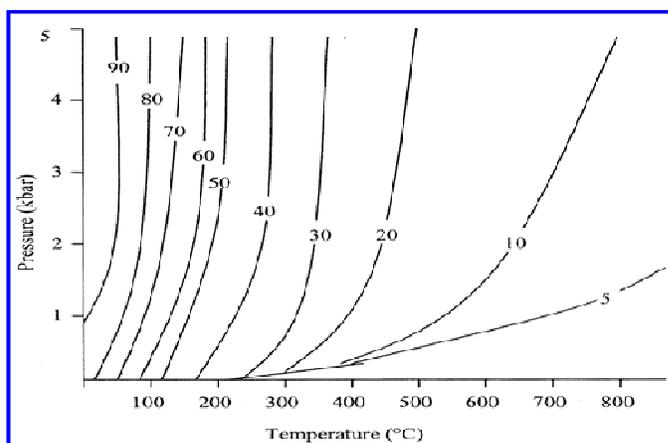


Fig 1.16. Variation of dielectric constant of water with temperature and pressure.

When the density of water is very high it can behave as non-aqueous fluid in which non-polar compounds may also dissolve completely.⁷⁵

1.6.4. Thermodynamic aspects of the Hydrothermal Growth of Crystals

When the process of crystallization takes place from the saturated solutions, the number of moles of solute and the free energy is represented as a function of temperature, pressure and number of moles:

$$G = f(T, P, n_1, n_2, \dots, n_i) \quad (5)$$

$$\begin{aligned} \partial G = & (\partial G / \partial T)_{P, n_i} dT + (\partial G / \partial P)_{T, n_i} dP + (\partial G / \partial n_1)_{P, T, n_j} dn_1 + \\ & (\partial G / \partial n_2)_{P, T, n_j} dn_2 + \dots \end{aligned} \quad (6)$$

where n_i is number of moles of the i^{th} the components and n_j is the constant number of moles of all the components except the component whose number of moles changes. The terms like $(\partial G / \partial n_2)_{P, T, n_j} dn_2$ means that P , T and all other mole numbers except n_2 were kept constant during differentiation. Such terms are called chemical potential,

$$(\partial G / \partial n_i)_{P, T, n_j} dn_i = \mu_i \quad (7)$$

At constant P and T , Eq (6) becomes:

$$\partial G_{P, T} = \mu_1 dn_1 + \mu_2 dn_2 + \dots = \sum \mu_i dn_i \quad (8)$$

On integration Eq (8) gives,

$$G_{P, T} = \mu_1 n_1 + \mu_2 n_2 + \dots = \sum \mu_i n_i \quad (9)$$

On differentiation Eq (9) gives

$$\partial G_{P, T} = \sum n_i d\mu_i + \sum \mu_i dn_i \quad (10)$$

By equating Eq (8) to Eq (10) yields,

$$\sum n_i d\mu_i = 0 \quad (11)$$

Eq (11) is considered as the overall equilibrium condition in the system with variable number of moles under constant P and T . In a hydrothermal system containing n_A mol of a solid A and partially soluble (n_{1A} mol) in n_B mol of a solvent B. Then the free energy of the system corresponds to Eq (9) as follows:

$$G = \mu_A n_A + \mu_{1A} n_{1A} + \mu_B n_B \quad (12)$$

If the process of dissolution of the solid components continues, then the free energy dG becomes,

$$G + dG = (n_A - dn_A)\mu_A + (n_{1A} + dn_A)dn_{1A} + n_B\mu_B \quad (13)$$

This change in the free energy under constant P and T becomes,

$$dG = (\mu_{1A} - \mu_A)dn \text{ or } dG/dn = (\mu_{1A} - \mu_A) \quad (14)$$

If $\mu_{1A} < \mu_A$, then dG/dn is negative and the process occurs on its own. When $\mu_{1A} > \mu_A$, the crystallization of the substance from solution takes place and the chemical potential decreases and when $\mu_{1A} = \mu_A$, the process reaches the equilibrium state. Consequently, the solute changes its phase from higher chemical potential to lower chemical potential. The phase transition stops when the chemical potential of both the phases becomes equal.⁷⁶ It is observed that the above considered mechanism is realized only when, in the non-equilibrium process, the changes in dG do not depend upon the chemical potential and concentration of other components of the solution. However, consideration of the above relationship may help in understanding the physico-chemical principles of the hydrothermal process.⁷⁶

1.7. Advantages of hydrothermal method:

Hydrothermal synthesis of single crystals of hybrid complexes offers numerous advantages over conventional and other known synthetic methods. The costs of instrumentation, precursors and energy are quite less in hydrothermal methods compared to many advanced methods. This method is environmentally benign and comparatively low reaction temperatures avoid problems like poor stoichiometric control and stress-induced defects that are encountered with high temperature methods, *viz.*, Bridgeman and Czochralski method. The rate and uniformity of nucleation, aging and growth that affects size, aggregation control and morphology is possible with this method. This method provides powders with controlled morphology and size is lucrative to industries like pigments, materials, medical diagnostics, pharmaceuticals, *etc.* Materials synthesized using hydrothermal method exhibit incongruity in point defects compared to materials synthesized by high temperature synthetic methods.

One of the major advantages of this method is that it can be easily hybridized with other methods like electrochemical, microwave, mechano-chemistry, ultrasound, hot-pressing and optical radiation to enhance reaction kinetics and increased ability for making new materials. This is a facile method which does not need catalyst, any seed, expensive and harmful surfactants or templates and thus promises for and low-cost, largescale production of high-class pure crystals.

1.8. Brief literature survey

The "hydrothermal" term is of geologic origin. Hydrothermal growth of crystals⁷⁷ was first reported by Karl Emil von Schafhäütl in 1845 when microscopic quartz crystals were grown in pressure cooker. Robert Bunsen in 1848 reported growth of barium and strontium carbonate crystals at 200 °C and 15 atmospheres pressure in a sealed glass tube and aqueous ammonium chloride as a solvent.⁷⁸ Crystals of various minerals were produced using hydrothermal synthesis by Henri Hureau de Sénarmont in 1849 and 1851.⁷⁹⁻⁸¹ Later in 1905, Giorgio Spezia reported the growth of macroscopic crystals⁸² using solutions of sodium silicate, natural seed crystals heated in a silver-lined vessel to 320-350 °C (one end present at top) and to 165-180 °C (other end at the bottom) 15 mm of new growth was obtained over 200-day period. A shortage of natural quartz crystals in the electronics industry during World War-II led to commercializing culture of quartz crystals using hydrothermal process by A. C. Walker *et. al* in 1950⁸³ The notable contributions have also been made by Nacken (1946), Hale (1948), Brown (1951), and Kohman (1955).⁸⁴

The history of "hybrid network" started in early 20th century. Werner extensively investigated coordination compounds in the early 20th century, and his pioneering Work was recognized and he was rewarded with Nobel Prize in Chemistry in 1913.⁸⁵ Coordination compounds with fascinating infinite structures are called hybrid networks, a term which appeared in early 1960's. In 1964, hybrid networks were reviewed by Bailar.⁸⁹ More hybrid networks have been discovered and studied by chemists since 1970. The term, "organic-inorganic hybrid materials" appeared in the early 1990's and this term were introduced by Hoskins and Robson in 1990's.⁸⁶⁻⁹³

Table 1.2. Development of the hydrothermal method.

Year	Focus	Remarks
1850-1940	Mineral synthesis	
	Improvement in pressure and temperature condition	Lower growth rate
1940-1970	Phase diagram for natural mineral systems	PVT diagrams
	Synthesis of new inorganic materials	Hydrothermal synthesis
1980-1990	Variety of new/advanced material synthesis	Supercritical and subcritical hydrothermal synthesis
	Synthesis of inorganic-organic hybrid materials/ condensed materials/ phosphors	Solvothermal/microwave assisted/ionothermal/sonochemical/electrochemical synthesis

The field of crystalline inorganic-organic hybrid materials has developed rapidly because of the unique and diverse characteristics and properties of these compounds. Since the preparation of zeolite, using “organic templates”, the rewards of typical synthetic inorganic chemistry has moved towards the exploration of novel crystalline hybrid materials. The discovery of new materials and characterisation remains the forefront of synthetic material science. Understanding the crystal architecture of novel compounds has contributed greatly to both established and emerging materials for applications, for example, optical and magnetic applications. The key idea when developing the hybrid materials is to take advantage of the best properties of each component that forms the hybrid, trying to decrease or eliminate their drawbacks and getting, ideally, a synergistic effect which results in the development of innovative materials with new properties. D. Xiao and his group has reported hydrothermal synthesis of triclinic crystals of hybrid copper vanadate $[\{\text{Cu}(\text{phen})(\text{H}_2\text{O})\}_2\text{V}_4\text{O}_{12}]$ ⁹⁴ space group $P\bar{1}$ using V_2O_5 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, phen and water. The hybrid compound consists of a novel double-chain ribbon constructed from tetravanadate clusters linked through copper–organic complex fragments. Ye Junwei *et. al* synthesized helix like $[\text{Cu}(\text{NIPH})(\text{bpy})]$ ⁹⁵ hydrothermally using Cu (II) acetate, 2,2'-bipyridyl (bpy) and 5-

nitroisophthalic acid (H₂NIPH). Cu atoms are coordinated to NIPH and bpy ligands. The complex crystallizes in the space group P2₁/c and shows high thermal stability. Magnetic measurements indicated an antiferromagnetic behavior of compound. Mesa *et al.* has reported the synthesis of three-dimensional hybrid complex, Ni₃(C₄H₄N₂)₃(V₈O₂₃)⁹⁶ under mild hydrothermal condition, at 170 °C. A UV-visible spectrum shows the characteristic bands of the Ni(II) d⁸ -high-spin cation in a slightly distorted octahedral coordination. Magnetic measurements indicate the existence of antiferromagnetic interactions. Mehtap *et al.* has reported the hydrothermal synthesis of copper based hybrid complex [Cu(4,4'-bipyH)₃(4,4-bipy)][HPW₁₂O₄₀]₂.12H₂O.⁹⁷ Single crystal X-ray diffraction revealed that the novel compound composed of two Keggin polyoxoanion connected with Cu complex fragment in 3D through hydrogen bonding. Shu Kui Shi *et al.* has reported hydrothermal synthesis of bisupporting Keggin-type complex, {[Cu(phen)₂]₂[(HBW₁₂O₄₀)]}[CuCl₂(phen)]₂.2H₂O and characterized the compound using elemental analysis, IR spectroscopy, UV/Vis/NIR spectroscopy, powder and single crystal X-ray diffraction. The polyoxometalate consists of one Keggin-type [HBW₁₂O₄₀]⁻ core and two covalently linked copper(II) complex fragments [Cu(phen)₂]₂. The presence of π···π interaction and hydrogen bonds within the complex lead to a stable supramolecular structure. Cherni *et al.*¹³⁴ has reported the hydrothermal synthesis of monoclinic mixed-ligand copper(II) complex, [Cu(C₁₂H₈N₂)(NO₃)₂]_n⁹⁹ with space group P2₁/n. The Cu(II) ions are penta-coordinated giving distorted square-based pyramidal geometry in CuO₃N₂ environment. Kellett *et al.* reported the synthesis and characterization of a square-planar copper(II) complex, [Cu(ph)(*o*-phen)].2H₂O and studied its various biological activities.¹⁰⁰ Cu(DNBA)₂(H₂O)₂ and Cu(DAT)₂(DNBA)₂ [3,5-dinitrobenzoic acid(DNBA) and 1,5-diaminotetrazole (DAT)] has been synthesized and characterized by Zhimin *et al.*¹⁴⁶ In Cu(DNBA)₂(H₂O)₂, Cu(II) was found to be coordinated to a plane tetragon through four Cu(II) was found to be coordinated to oxygen atoms of two DNBA⁻ ions and two H₂O molecules while in Cu(DAT)₂(DNBA)₂ two oxygen atoms and two nitrogen atoms from different DNBA⁻ ions and DAT ligands. Catalytic properties of the complexes were also studied using DSC. The complexes were found to have potential applications as

additives in solid rocket propellants.¹⁰¹ Ibragimov *et al.* has reported the synthesis mixed-ligand complex $[\text{Cu}_2(\text{L})_2(\text{TEA})_2] \cdot [\text{Cu}(\text{TEA})_2] \cdot 2\text{H}_2\text{O}$ and a supramolecular compound $[\text{Ni}(\text{TEA})_2] \cdot 2\text{L}$ [where TEA represents triethanolamine and L represents 4-hydroxybenzoic acid]. In $[\text{Cu}_2(\text{L})_2(\text{TEA})_2]$, metal atoms have tetragonal bipyramidal elongated due to Jahn–Teller effect and octahedral in the complex. $[\text{Cu}(\text{TEA})_2] \cdot 2\text{H}_2\text{O}$. The structural units of both the complexes are linked in 2D through extensive hydrogen bonds.¹⁰²

From the literature survey it is evident that the hydrothermal synthesis of single crystals of metal-organic hybrid complex has become certainly a leading synthetic method over the years. This method can lead to the synthesis of hybrid materials of high purity with interesting and riveting structural features. The unique and riveting behavior of organic ligands under hydrothermal conditions may lead to diverse and immensely useful complexes in various fields.

1.13. Objectives and applications of this research work

Synthesis of dislocation free single crystals of hybrid materials involves both challenges and opportunities. The most important challenge is synthesizing hybrid combinations that keep or enhance the best properties of each component while eliminating their particular limitations, having the opportunity to develop new materials with synergistic behavior. This behavior leads to an improvement in performance or to the discovery of new complexes with fascinating properties. Therefore the main objectives of this research investigation are as follows:

- To synthesize dislocation free single crystals of metal-organic hybrid complexes using hydrothermal technique and to study the coordination behavior of organic ligands under hydrothermal condition.
- To characterize and study the properties/potential applications of the synthesized metal-organic hybrid complexes using various physicochemical techniques
- To compare hydrothermal and conventional method of synthesis of metal organic hybrid complexes.

This present dissertation includes a total of seven chapters including this introductory one. The experimental section is discussed under Chapter II wherein details of

chemicals and the various physico-chemical techniques used to study the synthesized complex were described. The synthesis, structural characterization and properties/potential applications of the synthesized complexes are discussed in Chapters III to VI, followed by concluding remarks in chapter VII.

References

- [1]. T. Kaino, B. Cai, and K. Takayama, *Advanced Functional Materials*, 2002, **12**, 599.
- [2]. P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, John Wiley & Sons, New York, NY, USA, 1991.
- [3]. B. K. Periyasamy, R. S. Jebas, and B. Thailampillai, *Materials Letters*, 2007, **61**, 7, 1489.
- [4]. R. W. Munn and C. N. Ironside, *Principles and Applications of Nonlinear Optical Materials*, Chapman and Hall, London, UK, 1993.
- [5]. J. Bardan, R. Hierle, A. Perigaud, J. Zyss, and D. J. Williams, *Nonlinear Optical Properties of Organic Molecules and Polymeric Materials*, vol. **223** of ACS Series, American Chemical Society, Washington, 1993.
- [6]. Web site visited: <https://www.ccdc.com.sc.uk/solutions/csd-system/components/csd> on 23.11.2018.
- [7]. V.F. Petrenko, R.W. Whitworth, *Physics of Ice*. Oxford University Press, 1999.
- [8]. J.R. Hook, H.E. Hall, *Solid State Physics, Manchester Physics Series (2nd ed.)*, John Wiley & Sons, 2010.
- [9]. R. West, *Basic Solid State Chemistry (2nd ed.)*, Wiley. p. 1. ISBN 0-471-98756-5, 1999.
- [10]. *International Tables for Crystallography, Volume A, Space-group symmetry*, 2006.
- [11]. R.G. Lerner and G.L. Trigg, VHC publishers, *Encyclopedia of Physics (2nd Edition)*, 1991.
- [12]. N. Ashcroft and D. Mermin, *Solid State Physics, Brooks/Cole (Thomson Learning, Inc.)*, 1976.
- [13]. J. C. Brice, *The Growth of Crystals from Liquids*, North Holland, Amsterdam 1973.

- [14]. K. Fujiwara, K. Nakajima, T. Ujihara, N. Usami, G. Sazaki, H. Hasegawa, S. Mizoguchi and K. Nakajima, *J. Crystal Growth*, 2002, **243**, 275.
- [15]. A. A. Chernov in E. Kaldis (ed.), *Crystal Growth of Electronic Materials*, Elsevier, Amsterdam, p. 87, 1985.
- [16]. A. A. Chernov, *Modern Crystallography III*, Springer Verlag, Berlin, 1984.
- [17]. J. C. Brice, *J. Cryst. Growth*, 1975, **28**, 249.
- [18]. J. C. Brice, J. M. Robertson, W. T. Stacy and J. C. Verplanke, *J. Cryst. Growth*, 1975, **30**, 66.
- [19]. G. Muller in R. Fornaci and C. Paorici (eds.), *Theoretical and Technological Aspects of Crystal Growth*, Trans Tech Publ., Zurich, 1998, 87.
- [20]. P. Rudolph, M. Neubert, S. Arulkumaran and M. Seifert, *Cryst. Res. Technol.* 1997, **32**, 35.
- [21]. D. T. J. Hurle and B. Cockayne, *Handbook of Crystal Growth*, vol. 2a, North Holland, Amsterdam, 1994, 99.
- [22]. J. B. Mullin and K. A. Jackson, *Compound Semiconductor Devices. Structures and Processing*, Wiley-VCH, Weinheim, Germany, 1998, 1.
- [23]. P. Rudolph and M. Jurisch, *J. Cryst. Growth* 1999, **198**, 325.
- [24]. P. Rudolph in M. Isshiki (ed.): *Recent Development of Bulk Crystal Growth*, Research Signpost, Trivandrum 1998, 127.
- [25]. McPherson and D. T. J. Hurle, *Handbook of Crystal Growth*, vol. 2a, North Holland, Amsterdam, 1994, 417.
- [26]. F. Rosenberger and R. Fornari, C. Paorici, *Theoretical and Technological Aspects of Crystal Growth*, Trans Tech Publ., Zurich, 1998, 241.
- [27]. H. J. Scheel, Fornari and C. Paorici, *Theoretical and Technological Aspects of Crystal Growth*, Trans Tech Publ., Zurich, 1998, 201.
- [28]. H. J. Scheel, Peter Capper and Peter Rudolph, *Crystal Growth Technology: Semiconductors and Dielectrics*. John Wiley & Sons, 2010, 177.
- [29]. C. B. Aakeroy, N. R. Champness, *Cryst. Eng. Comm.*, 2010, **12**, 22.
- [30]. A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.*, 2006, **128**, 3494.
- [31]. K. Uemura, R. Matsuda, *J. Solid State Chem.* 2005, **178 (8)**, 2420.
- [32]. J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater*, 2004, **73**, 3.

- [33]. Yu-Ri Lee, J. Kim and W.S. Ahn, *Korean J. Chem. Eng.*, 2013, 30(9), 1667.
- [34]. R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M.O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939.
- [35]. N. Stock, *Micropor. Mesopor. Mater.*, 2010,**129**, 287.
- [36]. Y.K. Hwang, J. S. Chang, S.E. Park, D. S. Kim, Y. U. Kwon, S. H.Jhung, J. S. Hwang and M. S. Park, *Angew. Chem. Int. Ed.*, 2005, **44**, 557.
- [37]. R. Kerner, O. Palchik and A. Gedanken, *Chem. Mater.*, 2001, **13**, 1413.
- [38]. S. E. Park, J. S. Chang, Y. K. Hwang, D. S. Kim, S. H. Jhung and J. S. Hwang, *Catal. Survey Asia*, 2004, **8**, 91.
- [39]. S. H. Jhung, J. S. Chang, J. S. Hwang and S. E. Park, *Micropor.Mesopor. Mater.*, 2003, **64**, 33.
- [40]. S.H. Jhung, J.H. Lee, J.W. Yoon, J. S. Hwang, S. E. Park and J. S.Chang, *Micropor. Mesopor. Mater.*, 2005, **80**, 147.
- [41]. K. K. Kang, C.H. Park and W. S. Ahn, *Catal. Lett.*, 1999, **59**, 45.
- [42]. S. H. Jhung, J. S. Chang, Y. K. Hwang and S. E. Park, *J. Mater.Chem.*, 2004, **14**, 280.
- [43]. T. Mateovic, B. Kriznar, M. Bogataj and A. Mrhar, *J. Microencapsulation*, 2002, **19**, 29.
- [44]. Y. P. Xu, Z. J. Tian, S. J. Wang, Y. Hu, L. Wang, B. C. Wang, Y. C.Ma, L. Hou, J. Y. Yu and L.W. Lin, *Angew. Chem. Int. Ed.*, 2006, **45**, 3965.
- [45]. K. S. Suslick, D. A. Hammerton and R. E. Cline, *J. Am. Chem. Soc.*, 1986, 108, 5641.
- [46]. N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933.
- [47]. W. J. Son, J. Kim, J. Kim and W. S. Ahn, *Chem. Commun.*, 2008, 6336.
- [48]. U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, *J. Mater. Chem.*, 2006, **16**, 626.
- [49]. U. Mueller, H. Puetter, M. Hesse and H. Wessel, *PCT Patent*, 2005, **49**, 892.
- [50]. A. Lazuen-Garay, A. Pichon and S. L. James, *Chem. Soc. Rev.*, 2007, **36**, 846.
- [51]. H. Sakamoto, R. Matsuda and S. Kitagawa, *Dalton Trans.*, 2012, **41**, 3956.
- [52]. T. Friši, and L. Fábíán, *CrystEngComm.*, 2009, **11**, 743.
- [53]. T. Friši, *J. Mater. Chem.*, 2010, **20**, 7599.

- [54]. D. Zhao, D. Yuan and H. C. Zhao, *Energy Environ, Sci.* 2008, **1**, 597.
- [55]. P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux and R. Gref, *Nature Mater.*, 2010, **9**, 172.
- [56]. P. Horcajada, C. Serre, G. Maurin, A. N. Ramsahye, F. Balas, M. Sebban, F. Taulelle and G. Ferey, *J. Am. Chem. Soc.*, 2008, **130**, 6774.
- [57]. S. Freiberg and X. X. Zhu, *Int. J. Pharmacol.*, 2004, **282**, 1.
- [58]. K. S. Soppimath, T. M. Aminabhavi, A. R. Kulkarni and W. W. Rudzinski, *J. Controlled Release*, 2001, **70**, 1.
- [59]. Horcajada, P.; Serre, C.; Vallet-Regi, M.; Sebban, M.; Taulelle, F.; Ferey, G. *Angew. Chem. Int. Ed.*, 2006, **45**, 5974.
- [60]. K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H. C. Chang and T. Mizutani, *Eur. J. Chem.*, 2002, **8**, 3586.
- [61]. B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and B. E. Lobkovsky, *Adv. Mater.*, 2007, **19**, 1693.
- [62]. O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861.
- [63]. T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651.
- [64]. G. Ferey, *Chem. Mater.*, 2001, **13**, 3084.
- [65]. J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8329.
- [66]. S. Y. Yang, L. S. Long, Y. B. Jiang, R. B. Huang and L. S. Zheng, *Chem. Mater.*, 2002, **14**, 3229.
- [67]. K. Schlichte, T. Kratzke and S. Kaskel, *Micropor Mesopor Mater.*, 2004, **73**, 81.
- [68]. B. L. Karger, L. R. Snyder, C. Horvath, *An Introduction to Separation Science*, Wiley, New York. **1973**.
- [69]. U. Mueller, M. Hesse, H. Puetter, M. Kamieth and A. Schierle, *Patent*, WO 2006.
- [70]. G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191.
- [71]. R. A. Fischer and C. Woll, *Angew. Chem. Int. Ed.*, 2008, **47**, 8164.
- [72]. Y. E. Cheon, and M. P. Suh, *Chem. Commun.*, 2009, **45**, 2296.

- [73]. M. Uematsu, W. Harder and E. U. Franck, *The Dielectric Constant of Water, Technical Paper* 38p (WLKg. Gp. 3), Int. Assoc. for Prop., of Stern. Inter. Mtg. Kyoto Mtg. Jpn. 1976.
- [74]. P. Papon, J. Leblond, P.H.E. Meijer, *The Physics of Phase Transition: Concepts and Applications*, 2002, Berlin:Springer. ISBN 3-540-43236-1.
- [75]. S.D. Haman, *Physics and Chemistry of the Earth*, 1981, 13/14, 89.
- [76]. Hydrothermal Growth of Crystals, (K. Byrappa, ed.) *Prog. Crystal Growth Charact. Mater.* 1991, **21**, 1.
- [77]. W. S. Cho, M. Yashima, M. Kakihana, A. Kudo, T. Sakata, M. Yoshimura, *Appl. Phys. Lett.*, 1995, **66**, 1027.
- [78]. R. Bunsen, *Annalen der Chemie und Pharmacie*, 1848, **65**, 70.
- [79]. de Sénarmont *Comptes rendus* 1849, **28** : 693.
- [80]. H. de Sénarmont *Comptes rendus* 1851, **32** : 762.
- [81]. Hydrothermal Crystal Growth - Quartz Roditi International. Retrieved 2006-11.
- [82]. Giorgio Spezia, *Atti della Reale Accademia delle scienze di Torino (Proceedings of the Royal Academy of Sciences in Turin)*, 1905 **40**, 254.
- [83]. McWhan, Denis McWhan, *Sand and Silicon: Science That Changed the World. Oxford Univ. Press.* 2012, 11.
- [84]. R.A. Laudise, R.H. Doremus, B.W. Roberts and D. Turnbull, eds. *Growth and perfection of crystals. Proceedings of an International Conference on Crystal Growth held at Cooperstown, New York on August 27–29, 1958.* Wiley, New York. 1958, 458.
- [85]. A. Werner, http://nobelprize.org/nobel_prizes/chemistry/laureates/1913/werner-lecture.html 1913.
- [86]. J. C. Bailar, *J. Inorg. React.* 1964, **1** (1).
- [87]. B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.* 1990, **1**, 60.
- [88]. R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.* 1990, **23**, 1677.
- [89]. R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.* 1990, **10**, 762.

- [90]. M. J. Grannas, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.* 1990, **22**, 1644.
- [91]. B. F. Hoskins, C. J. McKenzie, R. Robson and L. Zhenrong, *J. Chem. Soc., Dalton Trans.* 1990, **9**, 2637.
- [92]. B. F. Hoskins, R. Robson and P. Smith, *J. Chem. Soc., Chem. Commun.* 1990, **6**, 488.
- [93]. A. K. Cheetham and C. N. R. Rao, *Science*, 2007, **318**, 58.
- [94]. Dongron Xiao, Haiyan An, Enbo Yang, Chunyan Sun, Lin Xu, *J. Coord. Chem*, 2006, 8.
- [95]. Y. Junwei, Z. Ping, Y. Kaiqi, Y. Ling , Y. Guangdi, W. Yue. *Chinese Science Bulletin*, 2006, **14**, 1682.
- [96]. Edurne S. Larrea, José L. Mesa and María I. Arriortua, *Materials Research Bulletin* 2011, **46(6)**, 845.
- [97]. Mehtap, Emirdag-Eanes, BanuÖnen, *Inorganic Chemistry Communications*, 2013, 38, 83.
- [98]. Shu Kui Shi, Zhan Guo, Rui Feng, Lin Yu Jin, *Zeitschrift fur Naturforschung B* , 2018, **73**, 3.
- [99]. S. N. Cherni and A. Driss, *Journal of Structural Chemistry.*, 2017, **58**, 194.
- [100]. A. Kellett, O. Howeb, M. Connor, M. McCann, B. S. Creaven, S. McClean, A. Foltyn-ArfaKia, A. Casey, and M. Devereux, *Free Radical Biol. Med.*, 2012, **53**, 564.
- [101]. Z. Li , Y. Yuan , Y. Zhang, L. Liu and S. Zhang, *J. Inorg. and Gen Chem.*, 2017, **643**, 647.
- [102]. A. B. Ibragimov, Zh. M. Ashurov, A. B. Ibragimov, B. S. Zakirov Russian Journal of Inorganic Chemistry, 2017, **4**, 439.