Chapter - 1

Introduction to Metal malonates and Crystal Growth

1.1 Metal Malonates

Carboxylic acids like formic, oxalic and malonic acids form salts with metal ions. Metal carboxylates evoke renewed research interest not only due to the wide range of applications but due to the variety of bonding modes – ionic, unidentate, chelating and bridging bidentate – exhibited by them. Mehrotra and Bohra [1] present a comprehensive account of the synthesis, physico-chemical properties, bonding and the numerous established uses of these compounds and their new derivatives. An interesting feature of the carboxylate bridge is that it can adopt diverse binding modes such as terminal monodentate, chelating to one metal center, bridging bidentate in syn-syn, syn-anti and anti-anti bridging tridentate to two metal centers. Carboxylates provide an efficient pathway that couples the magnetic centers either ferro- or antiferromagnetically, the coupling constant being influenced by the structural aspects [2-5].

Malonic acid (HOOC-CH₂-COOH) is a dicarboxylic acid, the next higher homologue of oxalic acid (HOOC-COOH). The methylene group (-CH₂-) inserted between the proximal carbonyl group is fairly active. Malonic acid exhibits different coordination modes to the same metal and the polymorphism of the coordination compounds is well-explored [6]. Malonic acid is of considerable biological importance. Release of malonic acid by plant roots, bacteria and fungi yields appreciable concentrations in soil interstitial waters [7].

Malonates are salts of malonic acid (1, 3 propanedioic acid) with a fairly active methylene group between the carboxylic groups. The methylenic H – atoms in malonic esters are acidic and often susceptible to attack by a suitable base and can be replaced by metal ions like Sr⁺, Mn⁺ etc. The salts of malonic acid have not only several hydrate forms but also structural modifications of the same compound. Metal complexes containing malonates arouse interest due to the
importance of their interactions in a wide variety of metalloproteins [8-12]. Malonate occurs naturally in biological systems and plays a vital role in symbiotic nitrogen metabolism and brain development. Bacterial assimilation of malonate through its decarboxylation and the inhibition of succinate oxidation by malonate have been explored for therapeutical purposes [13, 14].

1.1.1 Malonate dianion – a versatile ligand

The malonate ion (OOC CH₂ COO⁻) is a chelating, bidendate dicarboxylic ligand exhibiting diverse coordination modes and flexible stereochemistry [15]. It is a simple but very appealing and versatile dianion widely used for designing compounds with desired magnetic properties and in the design of molecular magnets [16, 17]. Catalina Ruiz-Perez and collaborators report on the construction of magnetic networks of 1D, 2D and 3D dimensionalities from malonato - bridged metallic complexes [18, 19]. The malonate derivatives of certain metals can provide the framework of supra molecular crystal engineering [20, 21]. The versatility of the malonate ligand is enhanced not only by the coordination and bridging modes exhibited, but also because its protonated species can afford complexes and mediate magnetic coupling between the magnetic centers [22]. Metal malonates thus arouse considerable interest amongst researchers due to their potential applications in molecular electronics, catalysts, biologically active-compounds and molecular-based magnetic materials. Malonates are vital intermediates in the synthesis of vitamins B₁ and B₆, barbiturates, non-steroidal anti-inflammatory agents and many other pharmaceuticals, agro chemicals and flavours [23 – 25].

1.1.2 Synthesis of Metal malonates

Metal malonates are synthesized by a number of pathways like fusion method, precipitation method, reactions in non-aqueous media and so on [26-30]. A conventional method is to utilize the reaction between malonic acid and metal hydroxide in an aqueous solution. The metal malonate is precipitated by evaporation. Recrystallization of the salt is essential in this method in order to obtain the crystal in pure form. A more suitable method is to utilize the
neutralization reaction of malonic acid by metal carbonate. The metal carbonate is dissolved in an aqueous solution of malonic acid and allowed to evaporate for a period of one week or more. The yield of the desired salt can be enhanced by heating the solution to a temperature about 50°C and then allowed for slow evaporation. For the synthesis of certain salts of temperature sensitive anions, lower temperature up to 5°C is suited. Christagu and Anderson described in detail the variety of techniques for the synthesis of malonates and other organic salts of strontium [31].

1.1.3 Crystallization of Metal malonates

Metal malonates have drawn much attention because of their intriguing structural complexity and potential applications in molecular electronics, catalysts, supramolecular crystal engineering molecular-based magnetic materials and so on. The reports on synthesis and studies of various metal malonates unveil the fact that the vast majority of them are prepared by precipitation or aqueous reaction methods. Precipitation is a fast crystallization process, often accompanied by agglomeration, which is undesirable. A crude precipitation process can be transformed into a crystallization process by careful control of the degree of supersaturation by exacting techniques which will yield defect-free single crystals. The demand for large, pure, defect-free single crystals is ever-increasing with the rapid strides made in scientific and technological developments [32].

Among the different crystal growth techniques, gel method is a simple, elegant and room - temperature solution growth method yielding a variety of crystals. The gel medium acts like a three-dimensional crucible eliminating turbulence; yet imposing no strain on the crystals. The diffusion and reaction processes are controlled and larger crystals are grown than could be synthesized by normal reaction and precipitation techniques [33].

Literature survey unfolds limited number of reports on synthesis of metal malonates by gel technique [34-36]. In this context, an innovative attempt to
grow more metal malonate crystals in gel felt necessary. The pursuing efforts turned out fruitful by the synthesis of six metal malonates followed by their characterization studies.

1.2 Crystals and growth techniques

Crystals serve as building blocks of modern technologies like microelectronics, optoelectronics, computers, lasers, biosensors, radiation detection and nuclear science and so on. They are inevitable for innovative research for the advancement of the above technologies. Ever since the science of crystal growth and structural crystallography emerged in 17th century, extensive investigations have been carried out to develop defect free single crystals. A rapid progress was achieved in 1912 when Max Von Laue and subsequently W. L Bragg successfully utilized the x-ray diffraction technique in the analysis of crystals. It was only after 1930 that understanding of crystal growth mechanisms at atomistic level started. The development of solid state devices was remarkably enriched due to the advent of the transistor in 1948. Crystal growth now embraces an immense field of materials and technologies [37]. Ever increasing applications in solid state physics demands the growth of high quality semiconducting, ferroelectric, piezoelectric and nonlinear optical (NLO) crystals.

Revolutionary advances in various fields were achieved by using single crystals [38]. The technological applications of crystal Physics are mainly three - fold: 1) High frequency techniques with the use of piezoelectric crystals (for the construction of frequency - dependent devices and ultra sound technology). 2) Semiconductor technique with the development of transistors and IC’s based on crystalline devices in information transmission and computer technology. 3) Laser techniques in the fields of optical measurement devices, chemical analysis, material processing, surgery and so on. The various possibilities of converting solar energy into electrical energy using crystals are of current global interest.
1.2.1 Crystal growth technology

A. Verneuil (regarded as the father of crystal growth), in 1902 achieved control of nucleation and thereby synthesized single crystals of ruby and sapphire. Now more than 20,000 tonnes of crystals are produced per year, the largest share being for semiconductors. Apart from the fundamental theoretical and experimental crystal growth studies, industrial fabrication of single crystals and their machining and characterization are the two major areas of crystal growth [39]. Crystal growth is now an interdisciplinary subject encompassing Physics, Chemistry, Materials Science, Metallurgy, Mineralogy etc. Demand of high quality semiconductor crystals has been increasing due to the ever expanding electronic and optoelectronic applications.

1.2.2 Crystal growth phenomena

The phenomenon of crystal growth is a process of ordering, thereby randomly arranged ions, atoms or molecules in the gas or liquid phase attain regular and orderly positions in the solid phase. The attainment of super saturation or super cooling is the pre requisite for any crystallization process. This is followed by two basic steps – formation of crystal nuclei (nucleation) and successive growth of crystal to get distinct faces [40].

1.2.3 Nucleation and growth kinetics

It is a vital phenomenon and the precursor of the overall crystallization process. Few solid bodies, embryos or seeds termed as ‘nuclei’ act as centers of crystallization. The primary stage in the process of crystal growth is nucleation. Nucleation occurs spontaneously or induced artificially by some external stimulus. Nucleation can be induced by agitation, mechanical shock, friction, high pressure, electric and magnetic fields, spark discharges and electro magnetic radiation. The above two types, called homogenous and heterogeneous nucleation respectively belong to the primary nucleation. Secondary nucleation refers to the phenomenon of nuclei generated in the vicinity of crystals present in a super saturated system [33].
Gibbs concluded that nucleation phenomenon was due to heterophase fluctuation in a supersaturated homogeneous phase [41]. Wulff, Volmer and Weber also followed the same ‘phase’ approach in their fluctuation theory of nucleation kinetics. Later Kossel and Stranski explained both equilibrium and growth of crystals using atomistic version of Thomson – Gibbs formula. The Burton, Cabrera and Frank (BCF) approach helped to broaden the nucleation concepts on various fundamental problems, such as morphological stability, dendritic growth and so on. The advent of modern computer technology could simulate the molecular systems and process, paving way to modern atomistic approach of growth kinetics [42].

The overall excess free energy ($\Delta G$) between a small solid particle of solute and the solute in solution is

$$\Delta G = \Delta G_v + \Delta G_s + \Delta G_e$$

where $\Delta G_v$ is the free energy change involved in phase transition, $\Delta G_s$ - free energy change involved in the formation of the free surface and $\Delta G_e$ the free energy change due to the elastic strain in the cluster (negligible). Hence the Gibbs free energy changes associated with a spherical embryo of radius $r$ is

$$\Delta G = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta g_v$$

where $\Delta g_v$ is the free energy change of the transformation per unit volume and $\sigma$ is the interfacial tension (surface energy) or the interfacial energy per unit area of the surface created. The surface energy term is always a positive quantity while the volume energy is a negative quantity in a supersaturated or super cooled system. The surface energy term increases with $r^2$ whereas the volume energy term decreases with $r^3$. Fig. 1.1 depicts the graphical representation of the expression, with the plots showing the dependence of surface energy change $\Delta G_s$, volume energy change $\Delta G_v$ and the net free energy $\Delta G$ on the size, $r$ of the nucleus.
\[ \Delta G = 4\pi\sigma \]

\[ \Delta G_v = \frac{4}{3}\pi r^3 \Delta g_v \]

**Fig. 1.1** Free energy diagram for nucleation explaining the existence of a 'critical nucleus'

\( \Delta G \) increases with increase in size, attains a maximum value \( \Delta G^* \) for radius \( r^* \) and then decreases for further increase in nuclear size. The size of the nucleus corresponding to the maximum free energy change is called critical nucleus [40]. The newly formed cluster is unstable when its size is less than \( r^* \) while it is stable when its size is greater than \( r^* \).

The critical size of the nucleus is found by setting the first derivative equal to zero, with the result

\[ r^* = \frac{-2\sigma}{\Delta G_v} \]

\[ \Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2} \]

Using Gibbs-Thomson relation, the equation yields to

\[ \Delta G^* = \frac{16\pi\sigma^3\gamma^2}{3(kT\ln S)^2} \]
where $S$ is the degree of supersaturation, $k$ – Boltzmann constant and $V$ – the molecular volume.

The rate of nucleation (number of nuclei formed per unit volume per second) can be expressed as

$$J = J_0 \exp \left( -\frac{\Delta G^*}{kT} \right)$$

where $J_0$ is the total number of particles in the new phase.

By substituting for $\Delta G^*$

$$J = J_0 \exp \left( -\frac{16\pi^3V^2}{3k^3T^3(\ln S)^2} \right)$$

The expression shows that the temperature, degree of supersaturation and interfacial energy influence the rate of nucleation.

1.2.4 Crystal Growth Theories

A critical nucleus of microscopic size, once developed (nucleation), under suitable conditions proceeds to grow to an optimum size. Nucleation and the growth kinetics are rather complex and many theories are proposed to explain the phenomena [39].

1.2.4.1 Surface Energy theory

Gibbs considered the growth of a crystal analogous to the growth of a water droplet in a mist. As all thermodynamical processes strive to minimize the free energy, atoms and molecules when they are in an orderly three-dimensional crystal structure try to achieve Gibbs free potential. If the volume free energy per unit volume is assumed to be constant throughout the crystal,

then $\Sigma a_i g_i = \text{minimum}$, where $a_i$ is the area of $i^{th}$ face of a crystal bounded by $n$ faces and $g_i$ is the free energy per unit area of the $i^{th}$ face. Thus when a crystal is allowed to grow in a supersaturated medium, the development of the various
faces should be such that the crystal has a minimum total surface free energy for a given volume.

Following Gibbs, Curie and Wulff derived an expression for the equilibrium shape of a single crystal based on Gibbs-Curie-Wulff’s theorem stating that in equilibrium the distances of the crystal faces from a point within the crystal (called a Wulff’s point) are proportional to the corresponding surface energies of these faces [43].

Marc and Ritzel suggested that when the difference in solubility is small, growth is mainly controlled by surface energy. Berthound and Valeton, on the basis of supersaturation suggested that the greater super saturation initiates rapid growth.

The surface energy theories still continue to be attractive, but it fails to explain the well-known effects of supersaturation and solution movement on the crystal growth rate [33].

1.2.4.2 Diffusion theory

This theory proposed by Noyes, Whitney and Nernst suggested that matter is deposited continuously on a crystal face at a rate proportional to the concentration difference between the deposition site and the bulk of solution [44]. The proposed equation of crystallization is

\[
\frac{dm}{dt} = k_m A (c-c^*)
\]  \( (1.8) \)

where \( m \) – mass of solid deposited in time \( t \), \( A \) – surface area of the crystal, \( c \) – solute concentration, \( k_m \) – coefficient of mass transfer, \( c^* \) - equilibrium saturation constant.

Nernst’s modified form of equation is

\[
\frac{dm}{dt} = \frac{D}{\delta} A (c-c^*)
\]  \( (1.9) \)
where $D$ - coefficient of diffusion of the solute, $\delta$ – length of the diffusion path.

Berthoud and Valeton revised the diffusion concepts and suggested that there were two steps in the mass deposition – a diffusion process, whereby solute molecules are transported from the bulk of the liquid phase to the solid surface, followed by a first-order ‘reaction’ when the solute molecules arrange themselves into the crystal lattice. These steps are represented by the equations

$$\frac{dm}{dt} = k_d A (c - c_i) \quad \text{(diffusion)} \quad \text{(1.10)}$$

$$\frac{dm}{dt} = k_r A (c_i - c^*) \quad \text{(reaction)} \quad \text{(1.11)}$$

where $k_d$ – a coefficient of mass transfer by diffusion, $k_r$ – a rate constant for the surface reaction. $c_i$ – solute concentration in the solution at the crystal - solution interface.

Recently Sobzak (1990) proposed an integral method to estimate the values of $k_d$ and $k_r$.

As a crystallization process is much more complex than the single two-step process envisaged by diffusion-reaction theories, new suggestions are proposed.

1.2.4.3 Adsorption layer theories

Volmer introduced the adsorption theory, and got modified by others. According to Gibbs – Volmer theory, when the units of the crystallizing substance arrive at the crystal face, they lose one degree of freedom and are free to migrate over the crystal face (surface diffusion). The absorption layer thus developed plays an important role in crystal growth and secondary nucleation. Once a layer is completed, a monolayer island nucleus, usually called a two-dimensional nucleus is formed.

The excess free energy of nucleation is
\[ \Delta G = a\sigma + V\Delta G_v \]  

where \( a \) is the area and \( V \) – volume of the nucleus and if this is a circular disc of radius \( r \) and height \( h \), the critical radius and the activation energy for two-dimensional nucleation are

\[ r_c = \frac{-\sigma}{\Delta G_v} \]  

\[ \Delta G_c = \frac{\pi \sigma^2 V}{kT \ln S} \]  

where \( S \) is the degree of supersaturation. From these, the expression for rate of nucleation and critical supersaturation can be obtained.

Kossel model envisages that an apparently flat crystal surface is made up of moving layers (steps) containing one or more kinks. Also, there will be loosely adsorbed growth units (atoms, molecules or ions) on the crystal surface and vacancies in the surfaces and steps [45].

![Fig. 1.2 A model of growth spiral steps with kinks](image)

A growth unit arriving on a crystal surface finds attachment sites such as terrace, ledge and kink (Fig. 1.2). It migrates towards a step and moves along it to a kink site and gets incorporated. From the attachment energy aspects, the most favorable face for growth can be determined.

Stranski postulated that the work necessary to detach a growth unit from its position on the crystal surface is the cardinal factor in growth process. Growth
units with highest detachment energy are energetically most favored for growth and vice versa.

Kossel, Volmer, Stranski model (KVS model) based on two-dimensional nucleation theory, could not explain the moderately high growth rates at low supersaturations. So some other mechanism may be responsible for the continuous growth of a crystal surface.

![Diagram of Kossel's model of a growing crystal surface](image)

**Fig. 1.3** Kossel’s model of a growing crystal surface

Frank [46] suggested that the presence of dislocation is the controlling factor in the crystal growth. A screw dislocation emerging at a point on the crystal surface functions as a continuous source of steps which can propagate across the surface of the crystal and promote crystal growth. Growth occurs by the rotation of the steps around the dislocation point. **Fig. 1.3** illustrates Kossel’s model of a growing crystal surface depicting flat surfaces (A), steps (B), kinks (C), surface-adsorbed growth units (D), edge vacancies (E) and surface vacancies (F). Later Burton, Cabrera and Frank (BCF theory) developed a kinetic theory of growth in which the curvature of the spiral near its origin was related to the spacing of successive turns and the level of super saturation. The dynamic process of spreading and bunching of growth spiral of mono-molecular height can be now observed in situ using atomic force microscopy (AFM) and scanning tunneling microscopy (STM) [47].
1.2.5 Crystal growth techniques

Crystal growth process is a phase transition phenomenon. Preparation of crystals can be achieved by the transport of crystal constituents in the solid, liquid or vapour phase [48]. Growth from liquid-to-solid phase has been further divided into two groups due to the distinct behaviour of melt and solution growth. Thus the crystal growth is basically classified into four categories:

- Solid state growth → Solid-to-solid phase transformation.
- Solution growth → Liquid-to-solid phase transformation.
- Melt growth → Liquid-to-solid phase transformation.
- Vapour growth → Vapour-to-solid phase transformation.

A brief discussion of the each growth technique is given below.

1.2.5.1 Solid state growth

This method is suitable for super ionic materials where the small cation is quite mobile. Usually, straining along with annealing is required to grow single crystals from a polycrystalline mass. Few metallic crystals are grown by solid state growth technique [49].

1.2.5.2 Growth from vapour phase

Growth of crystals from a vapour by direct condensation can be employed to produce small strain-free crystals of substances that sublime readily. Many metals and semiconductors of high melting point are crystallized by the method [33]. Vapour phase growth is basically of two types – physical vapour transport (PVT) and chemical vapour transport (CVT). PVT is use to synthesize materials having high vapour pressure at attainable temperature and CVT for relatively non-volatile materials [50, 51]. There are many modified versions of vapour phase method like MBE (Molecular beam epitaxy) and CVD (Chemical vapour deposition). These techniques are preferred for the fabrication of thin layers of metals, insulators and
semiconductors and there by find wide applications in electronics and optoelectronics industry. Chemical vapour deposition (CVD) is commonly used for growing thin crystalline layers directly from the gas phase [52, 53].

1.2.5.3 Growth from the solution

Solution growth is the widely used and the simplest method to grow many of the organic and inorganic crystals [54]. Solution growth may be classified into two – Low temperature solution growth and High temperature solution growth.

1.2.5.3.1 Low temperature solution growth

At a relatively low temperature, crystallization can be accomplished from a saturated solution in any of several ways: slow evaporation, slow cooling and diffusion method [55].

1.2.5.3.1a Slow Evaporation method

In slow evaporation, a saturated solution is kept under conditions where the solvent evaporates slowly. Rapid and gross super saturation can be prevented by providing mild mechanical shock or by seeding the solution with a few crystallites of the solute. This method, albeit simple, yields crystals of different materials and hence is used by many researchers [56-58]. Spontaneous nucleation leading to uncontrolled precipitation of multiple crystals causing defect formation is the main shortcoming of this method. Hence many modified versions are still being developed [59].

1.2.5.3.1b - Slow Cooling method

Another common solution growth technique is slow cooling. The saturated solution of the compound is heated of just boiling point and transferred to a Devar flask or thermostated oven and cooled at a specific rate of cooling. The cooling rate is controlled by surrounding this solution with sufficient insulating material. A variant of slow cooling is to establish a thermal gradient across the vessel containing solution. Crystallization occurs when the gradient is increased
by lowering the temperature of the heat sink. Horizontal and vertical gradient systems are made use of [60, 61].

1.2.5.3.1c - Diffusion method

Crystals can be grown by making use of diffusion in the liquid phase. When two solvents with a density difference are kept separated in vessel, as the solvents mix by diffusion, crystals appear at the interface between the solvents. The diffusion, in practice is effectively controlled in the presence of a gel medium. Gel aided solution technique has evolved as a versatile growth technique attracting the attention of many researchers [62-67]. A detailed discussion of this method is made in the following chapter.

1.2.5.3.2 High temperature solution growth

Low temperature solution growth often fails if the solubility in water is not high. However, at elevated temperature and pressure, many substances normally insoluble in water exhibit appreciable solubility. This property enables the growth technique, hydrothermal crystallization, which is carried out in steel autoclaves. Hydrothermal growth is employed for the synthesis of some important materials like sapphire (Al₂O₃), yttrium iron garnet (Y₃Fe₅O₁₂) and quartz.

Flux growth refers to the technique in which the molten salt solvents (flux) are used. This high temperature solution technique yields crystals of yttrium aluminum garnet (Y₃Al₅O₁₂), silicon, GaAs, InP, diamond and many other useful materials [68, 69].

1.2.5.4 Melt Growth

Crystallization can be accomplished in a pure melt in a similar manner to the growth from a super saturated solution. Semiconductor single crystals are produced from the melt at temperatures above 1420°C by defined control of the liquid – solid phase transition [70, 71]. The important melt growth techniques are
of four categories – the withdrawal or pulling techniques, the crucible methods, flame fusion and zone refining.

The **pulling techniques** are typified by the Czochralski and Kyropoulos methods. In both methods, a seed crystal is partially immersed in a melt, kept just above its melting point and growth is maintained just below the melting point by holding it on a water cooled rod or tube. The main difference between the two methods is that in **Kyropoulos technique** the seed is permitted to grow in the melt, while in **Czochralski technique**, the seed is withdrawn at a rate that keeps the solid-liquid interface almost in a constant position. Silicon, germanium, bismuth, tin, aluminum, zinc and many organic compounds are grown as strain-free single crystals by the pulling technique [33].

Bridgman and Stockbarger method is an example to **crucible method**. Here the melt is taken in a crucible with a conical bottom which is lowered from a hot to cold zone. The movement of the charge may be horizontal or vertical [72]. The gradient technique has proved successful for the growth of many semiconductors and alkali halides.

**Flame fusion technique** originally designed by Verneuil, has the advantage that no crucible is required. Here the crystal grows below a melt, which is fed from above. The method is presently used for the mass production of jewels (artificial gem stones) for watches and scientific instruments and of rubies for lasers.

**Zone melting** or zone refining technique was first applied to purify germanium for transistors. A molten zone is established at one end of the charge and advanced by moving either the container or the furnace. The method is best known as a purification method, as by repeated passage of the zone, the initial segment of the crystal becomes progressively purer. High purity crystals of silicon and refractory metals like tungsten and tantalum are synthesized by this technique.
1.3 Motivation and Objectives of the present study

The interest in the study of metal malonates stems from the uniqueness and versatility of malonate dianion as a ligand. Metal malonates, the salts of malonic acid thus arouse increasing attention due to their intriguing structural compositions and topologies offering enormous applications in electrical conductivity, molecular magnetism, host-guest chemistry, ion exchange, catalysis, pharmaceuticals, corrosion inhibition, supra molecular crystal engineering and so on. Syntheses of metal malonates by conventional methods are reported by many investigators; however limited attention is devoted in growing the corresponding single crystals. Literature survey thus reveals a gap between the studies on metal malonates and the synthesis of their large size crystals of superior quality.

The rapid strides in modern science and technology created a paradigm shift in crystal growth – a transition from ‘art’ to ‘science’. The demand for semiconductor materials with specific qualities boosted the crystal research interests, resulting in the bulk growth of large crystals and more recently in the synthesis of materials with nanometric dimensions. Crystals are conceived to be the unacknowledged pillars of modern scientific progress. Synthesis of good quality crystals with specific utilities has now got established as an indispensable processing technique.

Investigation on the growth of metal malonates by silica gel method was conducted due to the simplicity and versatility of this room-temperature solution method yielding a variety of defect- free crystals. Gel medium being chemically inert, prevents turbulence (convection) provides a three-dimensional structure which permits the reagents to diffuse at a desirable controlled rate. These factors prompted us to endeavor on the synthesis of metal malonates by single diffusion gel technique. Regarding the selection of cations (metals), it was envisaged to be from a broad span of metals in the periodic table – s,p and d group elements.
In the present work, six metal malonates – strontium malonate, manganese malonate, nickel malonate, copper malonate, cadmium malonate and lead malonate were to be prepared by single diffusion gel technique. Optimization of the various growth parameters – density of the gel, pH value, time of gellation, concentration of the reactants and period of crystallization is imperative. Various analytical tools like XRD, FTIR, FT Raman, thermal analysis, dielectric studies, DRS studies and magnetic studies will provide the characterization and the physico-chemical analysis of various properties of the grown crystals. The structures of metal malonates, as reported, are diverse. Cadmium malonate and copper malonate crystals are known to exhibit polymorphism – many structures and different hydrate forms. Thus the structural studies with the aid of powder XRD and single crystal XRD would facilitate in elucidating the interesting structures of the crystals. FTIR coupled with FT Raman studies unveil the presence various functional groups and bondings present in the materials under study. The thermal decomposition behaviour and presence of water molecules associated with each crystal can be investigated by the thermo-analytical techniques. The dielectric studies will provide an insight into the polarization processes that take place in the crystals. The energy band gap ($E_g$), the characteristic feature of the material can be extracted using DRS studies. The ability of malonate ligand to mediate significant ferro- or antiferro magnetic coupling between the paramagnetic centers sprouts the interest in the study of the magnetic behaviour of the grown crystals.

Obviously a study on the molecular bonding, thermal stability, dielectric properties, optical band gap and magnetic behaviour by the various analytical techniques will provide an in-depth understanding on the materials under investigation. Thus ‘Studies on certain gel-grown metal malonate crystals’ is expected to be an exciting challenge in the synthesis and studies of metal malonate crystals.
The objectives of the present work are shown in a nutshell.

**Objectives of the present work**

- Synthesis of six metal malonates – $\text{MC}_3\text{H}_2\text{O}_4.n\text{H}_2\text{O}$ (M = Sr, Mn, Ni, Cu, Cd, Pb) by single diffusion gel technique.
- Structural characterization of the gel-grown metal malonates using powder XRD and single crystal XRD studies.
- Analysis of the vibrational data from FTIR and FT Raman spectra and thereby to study the presence of various functional groups and coordination modes present in the samples.
- Investigation on the thermal decomposition behaviour of the materials using thermo-analytical techniques – TG, DTA and DSC.
- Analysis of the dielectric properties of the crystals as a function of temperature and frequency.
- Determine the energy band gap ($E_g$) of each material using diffuse reflectance spectroscopy (DRS) studies.
- Study the magnetic properties of the crystals using a vibrating sample magnetometer (VSM) at room temperature.
References


