Chapter - I

General Introduction

1. Introduction

_Crystals hanging in my window_
_Create an almost Heavenly sight_
_When the Sun comes pouring in,_
_Performing magic with its light._
_A hundred rainbows surround me daily_
_Just before the Sun goes down_
_And bring me joy beyond compare_
_As they dance around my walls of brown._
_Tiny fairies that one cannot catch,_
_Gentle breeze sets them to flight_
_Bringing smiles no matter what my day_
_Filling me with shear delight._

Christine B. (2010)

Due to the luster of crystal the poet experiences the heavenly sight, nowadays, the luster of crystals is in form of different applications and that has attracted the sight of scientists. Crystal is a solid material whose constituent atoms, molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions. The subject _crystal growth_ is a systematic study of the growth and properties of crystals. It is a multidisciplinary in nature. Crystal growth is a major stage of a crystallization process, and consists in the addition of new atoms, ions, or polymer strings into the characteristic arrangement of a crystalline Bravais lattice. The growth of crystals occurs either in nature or artificially in laboratory. The naturally grown crystals in the crust of Earth are the natural mineral crystals and can be considered as precious stones. Nowadays, the growth of crystals does not remain the phenomena only occurring in nature, but it has become a well advanced as well as widely used technology. A requirement of good quality crystals for the various applications is the demand of modern science and technology. This led the scientists to grow new variety of crystals. Recently, single crystal of silicon-28 grown in the most purest and perfect form polished in a perfect round shape balls to replace the
present standard of kilogram [1]. In spite of great technological advances the world is still at a developmental stage with respect to the growth of several important crystals.

The growth of crystal occurs not only in the crust of Earth or in laboratory but also in a living body. Many crystals, particularly, bio-materials and proteins, cause various ailments and health related problems. The urinary stones are usually composed of either pure or mixed crystals of calcium oxalate, brushite, struvite, hydroxyapatite and carbonate apatite [2]. Arthropathies, i.e., bone and joint diseases, are caused by crystals such as hydroxyapatite, calcium pyrophosphate and monosodium urate monohydrate [3]. There are other crystals which play important role in various ailments, for instance, f.c.c. type ferritin crystals in development of cataract [4] and cholesterol crystals for cardiovascular diseases and gall stones [5]. This bio-crystallization occurring in human body causes suffering and it is not desirable to occur. This has been discussed in detail by the predecessors of the present author [6-8]. There are several micro-organisms which synthesize crystals, for example, magneto-tactic bacteria synthesizing magnetite [9], chrysophytes [10] diatoms and actinopoda synthesizing siliconous materials and S. layer bacteria synthesizing gypsum and calcium carbonate surface layers [11]. Calcite crystals are found in mollusk shells [12] and as a component in gall stones [13].

The wide span of crystallization occurring from the Earth crust to living organism and finally in the laboratory, which requires multidisciplinary and multi-angle approach to study the phenomenon of crystal growth.

The crystal growth requires emphasis on the following three aspects, (I) Theory of nucleation and growth, (II) Experimental crystal growth, and (III) Characterization of crystals. Schieber [14] has well explained this in a schematic representation, which is shown in figure (1.1).
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Figure (1.1): Three aspects of crystal growth.

The earlier crystal growth study was divided into two parts:

1. The study of the equilibrium between the crystal and surrounding medium
2. The study of the kinetics of growth

Kossel model [15] is one of the most fundamental models to explain the crystal growth with the help of progressing steps having kinks on the crystal surface.

Volmer [16] considered the process of growth of a crystal surface as comprising of three main steps:

1. A transport of molecules from vapour to the adsorbed layer,
2. The diffusion of adsorbed molecules towards the steps and
3. The diffusion of adsorbed molecules along the edge of the steps towards kinks.

This is shown in figure (1.2).
Gibbs [17] developed a consistent phenomenological treatment (thermo-dynamic treatment) of the equilibrium problem, which is still essential as an introduction to the study of crystal growth by using analogy of liquid drop in a mist. Gibbs [17] and also Burton, Cabrera and Frank [18] investigated the conditions for nucleation and the requirements of critical nucleus for the further growth. Turnbull [19] proposed that the free energy of formation of a critical nucleus can be catalyzed by a suitable surface in contact with nucleus, which is known as a heterogeneous nucleation. Later on, Frank [20] and Burton [21] proposed the importance of dislocation, particularly screw dislocation, in crystals growth. This has been discussed in detail by Verma [22].

The demand of piezoelectric crystals has reached 4.8 billion US Dollars (USD) and it is further expected to increase 6.91 billion USD and nearly 750 different manufacturing companies are involved in the supply [23]. Silicon single crystals are generally grown for photovoltaic solar cells and silicon chips for device fabrications. In 2010 nearly 50,000 ton solar grade silicon was required for photovoltaic solar cell production [24,25]. The global silicon single crystal production is 10,000 tons per year [25]. Similarly, production of semiconducting III-IV (GaAs, GaP, InP, etc) single crystals, whose total cost exceeds 300 million USD is a dynamically developing bunch of world electronic industry. In Asian countries, particularly, in China the growth of semiconductor market is so high that it was positioned next to USA in 2010. As per one survey conducted by agency Frost and Sullivan, the total market of
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Semiconductor in India during 2006 remained 2.69 billion USD [26]. There is also a great demand for single crystal substrates, for example, sapphire single crystal substrates are used in LED and its demand has reached 4.2 billion USD worldwide [27]. Photonic Crystals are attractive optical materials for controlling and manipulating the flow of light. The global market for components and modules using Photonic Crystals indicates a CAGR (Compound Annual Growth Rate) of 33.1% and is estimated to reach $20.4 billion in 2017. The major drivers would be its applications having extra-ordinary growth, i.e., CAGR of 61.6% in Solar and PV cells and CAGR of 39% in LED segment with forecasts value of $4.1 Billion and $7.5 billion in 2017, respectively. The Photonic Crystals are seen as an alternative for semi-conductor fabrication; however, there would be a need for strong technological advancements to overpower the existing electronic segment. The semi-conductor foundry market has seen a 16.2% rise from 2011 to 2012 and reached $24.6 Billion value [28]. However, there are still large number of crystals awaits for large commercial applications, for instance, tartrate compound crystals. Notwithstanding, some applications of tartrate compound crystals are discussed in the end of this chapter.

The development and refinement of methods and of crystal growth processes to achieve useful products have relied heavily on empirical engineering and on trial and error method. Crystal growth still remains by and large an art rather than science, which has prompted Gilman [29] to select the title of his famous book, “The Arts and Science of Growing Crystals”. Crystal growth has been discussed by many authors in detail [22,30,31] as well as in Ph. D. theses of the predecessors of the present author [8,32,33] and hence it is avoided here.

The present thesis deals with the growth of various pure and mixed metal tartrate crystals by gel technique; hence details of the gel technique are discussed hereby. The subject of crystal growth in gels is not new. Indeed, it has enjoyed at least two long periods of popularity, one during the second half of 1800 and second roughly during the period 1913-1926 when the famous “Liesegang Rings” formed the main subject of interest, for example, the work of Liesegang [34], Bradford [35] and Holmes [36]. These intriguing and often beautiful periodic structures are frequently observed in nature and easily reproduced in laboratory. This has attracted the attention of well known German Chemist Ostwald [37] and Lord Rayleigh [38].
Larger crystals, several mm in size, were occasionally obtained but not systematically looked for. In contrast, the growth of such crystals is the principal objective of all the modern work in this field. An early claim made by Fisher and Simons [39] to the effect that “gels form an excellent media for the growth of crystals of almost any substance, under absolutely controlled conditions”.

There are good review articles and detailed reports available on gel growth technique by Henisch et al [40] and Patel and Rao [41]. Moreover, it has been explained and discussed very well by Henisch [42] in his famous book. The predecessors of the present author have discussed this technique in detail [8,43-45].

Even today the gel growth technique continues to attract various researchers. The gel growth is quite simple but an important technique, still it incorporates the arts and since of crystal growth. Nowadays, this technique is employed, for various reasons, to grow crystals of different interest and applications.

1.1 Gel Growth

A gel has been defined as "a two-component system of a semi-solid nature rich in liquid" [46]. According to the colloid chemistry definition, gels have a semi-solid consistency, and are stable in form, they are flexible, deform systems are produced by the interaction of a gel forming compound with the solvating medium. A characteristic property of gels is that they contain a conspicuously high percentage of solvent and little solid matter. The gel forming substances and solvating solvents stabilize each other in the gel structure and are the functional parts of one another. Gels may lose their solvent content during drying or dehydration and may pick up some spontaneously while swelling.

1.2 Types of Gels

Out of four states of matter - solid, liquid, gas and plasma, the three states of matter-solid, liquid and gas are more familiar. Even there are many exotic materials, which are having bizarre properties and find various applications. One of the exotic states of matter is gels. They are neither solids nor liquids. In early stage, gel has been defined as a two component system of a semi solid nature rich in liquid [46]. A gel may also be defined as a semisolid formulation having an external solvent phase, a polar (organo-gels) or non polar (hydro-gel), immobilized within the spaces available of a three dimensional networked structure [47]. Recently, according to IUPAC 2007
recommendations gel is defined as non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid [48]. A characteristic property of gel is that they contain a conspicuously high percentage of solvent and little solid matter. The gel forming substances and solvents stabilize each other in the gel structure. Most gels are mechanically and optically isotropic, except when under strain. As shown in Table (1.1), gels can be classified according to constituent (matrix) phase, solvent phase and cross-linkages.

**Table (1.1): Classification of gels**

<table>
<thead>
<tr>
<th>Classification of gel</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constituent Or Matrix Phase</strong></td>
<td><strong>Surfactant Bilayers</strong></td>
</tr>
<tr>
<td><strong>Solvent Phase</strong></td>
<td><strong>Solid - Liquid</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Solid – Gas</strong></td>
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<tr>
<td></td>
<td><strong>Solid - Solid</strong></td>
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<tr>
<td><strong>Cross-linkage</strong></td>
<td><strong>Physical Gel (Noncovalently Crosslinked Polymer Networks)</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Chemical Gel (Covalently Crosslinked Polymer Networks)</strong></td>
</tr>
</tbody>
</table>

### 1.3 Gel Structure

Gel may be formed either from a solution or from a solid substance exhibiting swelling power.

Two fundamental conditions must be fulfilled in order that a gel is formed from a solution.

(i) A solid substance shall be separated from the solution in a finely dispersed "Colloidal state", and
(ii) The separated solid particles shall neither be deposited by gravity nor remain in a colloidal suspension as freely moving kinetic units, but they shall join together to form a continuous coherent framework throughout the mass of the solution.

Any processes capable of producing the separation of solid phase, i.e., crystalline or amorphous, from a solution forms a gel. Therefore, a condition of supersaturation obtained by change in temperature, evaporation, addition of another substance (non-solvent or salt) or by chemical reaction is the first step. Secondly, the suitable condition allowing of the formation continuous pattern or framework of colloidal fineness is required.

The structure of synthetic and semi-synthetic gels is generally dependent on the chemical preparation of the basic substances, the relative concentration of the reagents and the solubility conditions during gel formation. The reactions inducing cross-linkages are random processes governed by the laws of statistical probability. These processes cause voids of dimensions and geometry characteristic of the type of gel used to form the polymer chains. These voids are known as the pore size of the gel. The pore size is one of the most important parameters of the molecular phenomena. Pore sizes may be influenced by the conditions of formation, and the solubility relationship of the initial substances and the end product.

From the aspect of pore sizes, it is possible to distinguish two principal types of gel structures, that is, microreticular (microporous) and macroreticular. The more uniform repetition of the cross links in microreticular gels produces smaller pores and renders the gel suitable for separation of smaller molecules. Micro-reticular gels are obtained if the solubility of the starting substances (monomers) and the end product do not differ greatly and if the cross links assume the desired gel structure only gradually, for instance, by increasing the number of cross-links between polymer chains already fixed.

The structure of the macro-reticular gels is rather heterogeneous and the spatial distribution of the matrix is uneven. Their large pores render them suitable for the permeation and separation of macromolecules [46].
1.4 Structure of Silica Hydro-Gel

Silica hydro-gel is the most favorite gel for the crystal growth experiments; hence the study of its gelling mechanism and gel structure carries considerable importance. When sodium meta-silicate goes into aqueous solution, mono-silicic acid is produced in accordance with the dynamic equilibrium,

\[
\text{Na}_2\text{SiO}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 2\text{NaOH}
\]

This mono-silicic acid can polymerize with the liberation of water,

\[
\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{Si} & \quad \text{Si} & \quad \text{Si} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\end{align*} + \quad \begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{Si} & \quad \text{Si} & \quad \text{Si} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\end{align*} \rightarrow \quad \begin{align*}
\text{Si} & \quad \text{Si} & \quad \text{Si} \\
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{Si} & \quad \text{Si} & \quad \text{Si} \\
\end{align*} \quad \text{OH} \\
\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

This can occur repeatedly and a three dimensional network of Si-O links is established as silica hydro-gel.

As the polymerization process continues, water accumulates on top of the gel surface. This phenomenon is known as “Syneresis”. Much of the water has its origin in the above condensation process, and some may arise from purely mechanical factors connected with a small amount of gel shrinkage. The well-known stability of the silicon-oxygen bonds is responsible for the fact that the polymerization is largely irreversible.

Recently, Vyas et al [49] have reported the role of sodium metasilicate and NaOH produced during gelation on crystal growth. Sodium metasilicate is not only supporting the growth but plays an important role in crystal growth. The simple reaction between two salts does not give precipitation but in the presence of sodium metasilicate solution or NaOH solution it gives precipitation. The authors have discussed in detail by taking example of growth of calcium tartrate crystals.
The time required for gelation is very sensitive to pH. As the gelation is a gradual process, there is no unique definition for gelation time. Between the chains the cross-linkages are formed in due course, and these contribute to the sharp increase of viscosity that signals the onset of gelation. Because of their low mobility, very long chains will cross-link more slowly than short chains. At very low pH values, the tendency towards polymerization is diminished and chain formation is slowed. Gelation time is strongly dependent on temperature \[46\]. This has been described in detail by Henisch \[42\]. Vyas et al \[49\] also reported that at very low pH the gel formation is not taking place. Parikh et al \[50\] reported the effect of pH on gelation time and number of grown crystals.

A weak acid is generally preferred to adjust the pH values, because pH of the set gel changes only slightly with time, and secondly, the mineral acids tend to spoil the growing crystals. It is noteworthy that in less acidic gel solutions the reaction between the acid and sodium meta-silicate occurs with liberation of hydroxyl ions and thus pH of the solution rapidly increases with the process of polymerization, while in highly acidic gel there is no change in pH except due to very little difference in dissociation of acids of different complexities, as well as requirements of reaction mechanism. Hence pH has profound influence on the gel structure \[51\].

1.5 Gel Growth Methods

Crystal growth in gel has been mainly divided into the following five different methods:
1. Reaction Method.
2. Chemical Reduction Method.
5. Electrolytic Method.

1.5.1 Crystal Growth by Reaction

Crystals which are insoluble or slightly soluble in water and decompose before reaching their melting points can be conveniently grown by this method. The basic requirements to grow single crystals by this method are:

(1) The reactants used must be soluble in the solvent (usually water) and the product crystal must be relatively less soluble.
(2) The gel must remain stable in the presence of the reacting solutions and must not react with these solutions or with the product formed.

(3) Some solubility of the product crystal is needed in order to grow crystals of any size [52].

Two aqueous solutions of soluble salts are suitably chosen and allowed to diffuse through the gel, so that there can be a slow and controlled segregation of ions and molecules resulting into the precipitation of an insoluble phase as the crystal. The gel affords to limit the number of critical size nuclei and decreases the rate of crystal growth either by controlling the diffusion of reacting ions or by governing the reaction velocity on the surfaces of the growing crystals.

Resulting chemical reaction can be expressed as:

\[ AX + BY \rightarrow AY + BX \]

where, A and B are the cations, X and Y are the anions.

This can be achieved by the test tube technique, in which one of the reactants is incorporated in the gel and the other reactant is diffused into it, or by the U-tube technique as shown in figure (1.3), in which the two reactants are allowed to react by diffusion into an essentially neutral gel.

![Figure (1.3): Crystal growth by reaction method](image)

### 1.5.2 Chemical Reduction Method

This method is suitable for growing only metal crystals from gel media. Hatschek and Simons [53] were the first to report the growth of gold crystals by
adding 8 % oxalic acid solution over a set gel containing gold chloride solution. By this particular method crystals of Nickel, Cobalt, Selenium, Lead and Copper have been obtained.

1.5.3 Complex Decomplexion Method

This method requires first forming a chemical complex of the material of the crystals to be grown with aqueous solutions of some suitable substance, called complexing agent, in which the former is homogeneously mixable and then providing externally a condition conducive to de-complexing or dissociation of the complex formed. A standard procedure adopted for decomplexion is to increase the dilution steadily, while complex solution is diffused through the gel. Crystal growth by this method was first attempted by O’ Connor et al [54] for the growth of cupric halide crystals.

1.5.4 Solubility Reduction Method

![Figure (1.4): Crystal growth by solubility reduction method](image)

In this method, the substance to be grown is dissolved in water and is incorporated with the gel forming solution. Then a solution, which reduces the solubility of the substance, is added over the set gel to induce crystallization as in figure (1.4). For instance, potassium dihydrogen phosphate (KDP) crystals have been grown by adding ethyl alcohol over the gel containing a saturated solution of KDP [55]. Crystals are grown due to the reduction of solubility of KDP in the liquid phase by the diffusing alcohol.

This method is applicable to grow single crystals of highly water-soluble substances. The growth of ammonium dihydrogen phosphate (ADP) single crystals by this method has been first reported by Gloker and Soest [56].

1.5.5 Electrolytic Method

The electrolytic method can also be used for the growth of metallic crystals by selecting the gel medium for controlled growth. In this method a very low dc electric
current, usually of the order of 2-10 mA, is passed through a silica gel charged with suitable acid or electrolytic solution.

Figure (1.5): Crystal growth by electrolytic method

Details are given in figure (1.5). It has been found that the pH of the gel medium, the concentration of the supernatant solution, the current density and the material used as electrode, have considerable influence on the habit of the crystals grown. Mohanan Pillai et al [57] grew lead dendrites, while George and Vaidya [58] grew copper dendrites and silver dendrites and single crystals using the electrolytic technique.

1.6 Modified Gel Growth Technique for the Micro-crystal Growth

The growth of micro-crystals is playing important role in various systems, including the human body. The modified gel growth method has been developed by Parekh et al [59] for the growth of micro crystals. This technique is comparatively rapid, requires less amount of reactants and in situ observations of the growth are possible. In the experimental technique for micro-crystal growth, glass slides with cover slips and Petri dishes are used as the growth apparatus. The glass slides are arranged in the Petri dish in form of a plus sign, where the lower slide is used just for the support and the upper slide is used for the micro-crystal growth. To grow the micro-crystals in a silica gel medium, a sodium meta-silicate solution of desired
specific gravity is mixed with weak acid so that appropriate pH could be set for the mixture. Thereafter, with help of suitable glass dropper a small drop of this mixture is put at the middle of glass slide. The cover slip is put on this drop of mixture in such a way that it floats on the mixture and covers almost the area of a cover slip size, without spillage beyond the cover slip. To assure that the gelling process occurs properly without drying the solution, the slides are put in a Petri dish in such a way that water poured in the Petri dish does not touch the cover slip, but remains slightly below the upper surface of the slide. After setting the gel, water is sucked from the Petri dish with the help of suitable dropper. Thereafter, other solution of appropriate salt is added with dropper carefully so that it should cover the slide up to the cover slip. The poured solution diffuses through the gel and a reaction takes place between the weak acid impregnated in the gel and the salt solution poured afterwards and, subsequently, nucleation and growth of micro-crystals occurs within 24 hours. Figure (1.6) describes this technique schematically.

1.7 Spherulitic Crystals

Spherulites were first observed by Bunn and Alcock in a polymer system in 1945 [60], however, Price [61] studied in detail about the kinetics of spherulitic formation. In most of crystal growth, after attaining a stable size a typical primary nucleus grows into a crystallite having a discrete crystallographic orientation. This continues to develop as a single crystal until it impinges either upon external boundaries or upon other similar crystallites advancing from neighboring nuclei. In certain systems, primary nuclei are incapable of such a development and each one
giving rise instead to a more complicated structure. It is with a radiating array of crystalline fibers, all having the same fiber axis. The fibers branching will be in such a way that the crystallographic orientation of a branch departs slightly, but appreciably from that of its parent fibers. It is a characteristic property of these particular systems that the primary nuclei initiate the formation of polycrystalline aggregates, which are more or less radially symmetric. The growths of these aggregates, which are called spherulites, occur naturally in silicate minerals and found in igneous rock strata. Apart from this, artificial spherulites have been grown in organic and inorganic compounds. High polymers from melt exhibit spherulitic habit [62]. According to McCauley et al [63] a spherulite is a crystalline spherical body, which is formed by the growth of radiating crystallites or a concentric banding, is a polycrystalline aggregate and not a single crystal.

Impurities may play a crucial role in promoting a fibrous habit in spherulitic crystallization, which has been suggested by Bernauer [64]. Buckley [65] suggested that impurity concentration in a crystalline phase might be one of the reasons for spherulitic crystallization. Spherulite forming minerals are multi-component system in which certain components are likely to be rejected preferentially by the crystals. If the crystallization can occur in the presence of another substance, the latter can be regarded as an impurity. Presence of quantities of free acid or alkali, which should make addition to the H⁺ or OH⁻ ions concentration, does not seem to make any difference to the large majority of crystals. However, according to one point of view, H⁺ and OH⁻ can be regarded as ever-present impurities in the strictest sense of term in aqueous solutions. Kurian and Ittyachen [66] have grown spherulitic crystals of some alkaline earth molybdates (BaMoO₄ and CaMoO₄) under controlled diffusion of reagents in silica gel media. They found that the pH value of media has predominant influence on crystallization. Also the effect of impurity and length of gel column found to be contributing much to the kinetics of growth. The authors acidified the gel by HNO₃. They ultimately conjectured that the spherulitic crystallization of BaMoO₄ in silica gel might be due to the presence of H⁺ ions in abundance.

Usually, the outer boundaries of spherulites are spherical, but some are irregular and oval in out line, especially, when they coalesce. The growth is constrained to 4π solid angle. The spherical structures of some of them have the
appearance of onion-like partings at the surface. Sometimes spherulites nucleated in a slightly acidic medium are affected by a kind of dissolution and natural etching [66].

Moreover, the mode of crystallization of the rare earth tartrates in gel has been discussed in detail by Raina [67]. The three zones, where distinct mechanism of crystallization becomes operative, were discussed as follows:

(1) The first zone is in the immediate vicinity of the gel – reactant interface (zone –A), where the upper (corresponding rare earth nitrate) and the lower (tartaric acid in gel) reactants come in immediate contact. As a consequence of instantaneous reaction between the two reactants, there is a rapid formation of a crust. The crust is observed to be a highly polycrystalline aggregate, gel having very little role to play in controlling the diffusion of the respective ions.

(2) The second operative mechanism is the crystallization of the rare earth tartrates out of their precipitate. The precipitate initially develops at the gel-reactant interface, grows with the passage of time over a few days and advances into the gel column. The advancement of the precipitate ceases after it attains some particular thickness. The precipitate zone at this stage is shown as zone BC in figure (1.7). The rate of advancement and the ultimate thickness of the colloidal precipitate depend on the concentration of the upper reactant.

![Figure: (1.7)](image-url)
(3) The third mechanism, by which crystallization of the rare earth tartrates become operative is in the zone CD, figure (1.7), which is at the bottom of the crystallizer. As it is indicated by the figure, only normal spherulites (without spikes) grow in this zone. This is unlike the precipitate zone where some of the spherulites develop spikes at a later stage of their growth. This mode of crystallization is thus in the clear zone of the gel column below the precipitate zone.

The spherulitic crystals of iron (II) tartrate, iron (II)-cobalt mixed tartrate and iron(II)-nickel mixed tartrate have been grown by Joseph [43], iron-nickel-manganese mixed ternary levo-tartrate crystals as well as iron-manganese-cobalt mixed ternary levo-tartrate crystals have been grown by Joshi et al [68,69]. The present author has obtained spherulitic crystals of lead and cobalt mixed levo tartrate, which is discussed in chapter-5.

1.8 Dendrite Crystals

Crystalline dendrites appear everywhere throughout the natural world in numberless branched forms, as diverse as snowflakes and frost patterns, or as minerals crystallized from solutions and magmas. Dendritic crystals are also prevalent in metallurgical technologies, including alloy casting, primary metals production, welding, and soldering. Dendrites in metallurgy establish the initial microstructures of cast metals and alloys, and are responsible for setting patterns of chemical segregation, crystallographic texture, and grain size developed in these materials.

The descriptive term “dendrite” derives from the Greek word for tree as “δενδρον”, particularly a tree with its highly branched trunk. A dendritic crystal will usually exhibit morphological hints of its underlying crystalline structure and symmetry, as it commonly consists of a primary stem, secondary arms or side branches, with tertiary branches sprouting from the secondary—all growing in selected crystallographic directions. It is the continuous generation of all these branches during dendritic solidification that establishes the ramified pattern, length scale, and spatial distributions of all the chemical components and impurities contained in a solidifying melt or solution.

Dr. James S. Langer [70], a prominent physicist has added much to the theoretical development of this field. His thoughtful reflections address the question of why achieving a fundamental understanding of this complex phenomenon still remains desirable and underscores its special relevance today for metallurgists.
attempting to improve alloys and cast materials design in general. Traditionally, the subject of dendritic growth theory is divided into the following two independent components: (1) transport theory, which explains how the large-scale energetic of the $l \rightarrow s$ transformation operates and controls the dendrite speed and size and (2) interface physics, which captures the underlying microscopic phenomena that are responsible for the branching and directionality that characterize dendritic patterns in real materials. The two theoretical components of dendritic growth have both markedly different histories and status with respect to modern experiments conducted on dendritic growth kinetics and morphologies.

Dendritic crystallization forms a natural fractal pattern. Dendritic crystals are formed from growth instabilities that occur when the growth rate is limited by the rate of diffusion of solute atoms to the interface. In this case, there must be a concentration gradient from the supersaturated value in the solution to the concentration in equilibrium with the crystal at the surface. Any protuberance that develops is accompanied by steeper concentration gradients at its tip. This increases the diffusion rate to the tip. In opposition to this is the action of the surface tension tending to flatten the protuberance and setting up a flux of solute atoms from the protuberance out to the sides. However, overall, the protuberance becomes amplified. This process occurs again and again until a dendrite is produced.

Often many crystals exhibit the fascinating dendrite-type or feather-type crystal growth, and it is found to be quite challenging to understand its mechanism. Fujiwara and Nakajima [71] studied the mechanism of dendrite crystal growth, whereas Kessler et al [72] considered in their model that each crystal has certain direction in which its growth is the fastest, and the dendrites grow in these directions. As the columns grow larger, their surfaces become flatter and more unstable. At faster growth rates, the instability is more likely to occur and gives dendritic growth.

Considering the numerical results, Li et al [73] have revealed that under anisotropic kinetic boundary conditions, a non-monotone temperature distribution forms on the surface that leads to oscillations of the scaled tip velocity. This dynamic process works like a limit cycle that generates a sequence of protuberances near the tip. These protuberances propagate away from the tip and develop into side branches at later times. Dendrite-type growth morphology has been observed by several authors
in the gel-grown crystals, such as ammonium tartrate [74], lead chloride [75], lanthanum tartrate [76], barium oxalate [77], strontium iodate [78], cadmium tartrate [79] and lead tartrate [80].

1.9 Tartrate Compound Crystals Grown by Gel Method

Numerous workers have grown various tartrate compound crystals by the gel growth technique. The predecessors of the present author have already done exhaustive literature survey of gel grown crystals [32,43-45] and hence the repetition is avoided. It is a tedious and laborious task to cover the entire list of crystals; nevertheless, some important crystals, grown during last five years are reported hereby.

Different crystals have been grown by the gel techniques and characterized by several authors recently, for example; growth of barium oxalate crystals in agar-agar gel and their characterization [81], growth and characterization of lead tartrate crystals [82], comparative study of pure and doped single crystals of lead iodide dihydrate and lead tartrate dihydrate grown in silica gel using Fourier Transform Raman Spectra [83], characterization of gel grown iron-manganese-cobalt ternary levo-tartrate crystals [69], study of gel grown strontium iodate [78], structural and optical properties of calcium cadmium tartrate [84], study of thermal and dielectric behavior of manganese malonate dihydrate single crystals [85], characterization of gel grown cadmium tartrate single crystal [86,87], growth and thermal behavior of mixed crystals of calcium cadmium tartrate in silica gels [88,89], four metal–organic coordination polymers in the forms of \([\text{Cd}_3(\text{C}_4\text{H}_4\text{O}_6)_3(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\)nI, \([\text{Cd}_3(\text{C}_4\text{H}_3\text{O}_6)_2(\text{H}_2\text{O})_2]\cdot 5.5\text{H}_2\text{O}\)nII, \([\text{Cd}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}\)nIII, and \([\text{Cd}(\text{C}_4\text{H}_4\text{O}_6)]\)nIV were obtained under hydrothermal conditions and characterized and revealed that compounds I–III exhibit new 3D open frameworks filled with water molecules [90] and FTIR and thermal studies of iron-nickel-manganese ternary levo-tartrate crystals [68].

Moreover, attempts have been made to grow and characterize mixed tartrate of different compounds crystals by several researchers, for instance; growth and characterization of iron (II)-cobalt levo tartrate and iron (II)-nickel levo tartrate [43], calcium-strontium levo tartrate [91], iron-manganese tartrate [92], manganese-strontium levo tartrate [93], manganese-iron-nickel, manganese-iron-cobalt and
manganese-copper mixed levo tartrate crystals [32]. Using gel growth technique to mimic the growth of biomaterials crystals in body, several biomaterials crystals have been grown, for example, urinary crystals [8] crystals responsible for arthritis [94] in the present author’s laboratory.

Very recently in the present year 2015, crystals of a new polymorphic modification of monobasic sodium tartrate monohydrate NaHC₄H₄O₆ · H₂O have been grown in a metasilicate gel and their atomic structure is solved by X-ray diffraction [95]. Also, Ahmed et al [96] have studied single crystal growth of lithium hydrogen tartrate by gel encapsulation technique and reported that the correlated barrier hopping is the dominant charge-transport mechanism.

To best of the present author’s knowledge no attempt is made to grow mixed levo tartrate crystals of lead-iron, lead-cadmium and lead-cobalt, which is discussed in detail in chapter 3, 4 and 5, respectively of the present thesis.

1.10 Advantages and Limitation of Gel Growth

Gel method has many advantages and it is preferred to grow the crystals, which are, otherwise, very difficult to grow by other techniques. This method is quite popular to grow crystals which are sparingly soluble in water or decompose on heating.

The gel framework, which is chemically inert and harmless, acts like a three dimensional crucible wherein the crystal nuclei are delicately held in the position of their formation and growth, thereby preventing the damage, if any, due to impact with either the bottom or the walls of the container. Also, the crystals can be observed practically in all stages of their growth. All crystal nuclei are spatially separated and hence the effects of precipitations are eliminated. The gel medium considerably prevents convection currents and turbulence.

Thermodynamic consideration reveals that as the growth proceeds at ambient temperature, the grown crystals would contain relatively less concentration of equilibrium defects.

In the gel growth technique, by changing the growth conditions, crystals with different morphologies and sizes can be obtained.

Inasmuch as this method is extremely simple and inexpensive, good quality crystals can be grown even in small laboratories, which do not possess sophisticated equipments, however, it requires delicate art of growing crystals.
With many advantages the gel growth method possesses several limitations also. Crystal size is generally small and the growth period is large, therefore, large crystals cannot be grown by this method. In case of using silica gel, the gel inclusion occurs during growth in some crystals. Also, there is a chance of lattice contamination by impurities from the gel itself.

1.11 Significance and aim of the Present Study

Compounds of tartaric acid find various applications in science and technology [97]. Many tartrate compounds have exhibited novel properties, which has lead to several applications, for example, piezoelectric application of cadmium tartrate [98], the addition of lead tartrate in gasoline to prevent knocking in motors [99], ferroelectric properties of sodium potassium tartrate [100] and ferroelectric, dielectric, optical and thermal properties calcium tartrate [101]. Several tartrate compounds deserve special attention due to their medical and pharmaceutical applications. For example, injections of Na-Cr tartrate, Na-Fe (III) tartrate and K-Cr tartrate increase the susceptibility of transplanted sarcoma to the effects of X-rays [102]. Iron tartrate complex ions play important roles as contrast blocks of renal tissues prior to their dehydration [103]. Iron tartrate is one of the prominent species in apple juice [104].

In wine industry certain tartrate compounds find applications and presence of certain compounds are unwanted, such as iron-tartrate is used as catalyst in champagne manufacture [105] and the formation of potassium hydrogen tartrate crystals in wine bottles is unwanted and efforts are made to avoid it by a trap process or by influence of external electric field [106].

There are certain tartrate compounds find applications in cosmetics. The synergist effect of tartaric acid for zinc ion in cosmetics has been reported [107]. Also, the tanning action of iron-tartrate to tan skin has been reported [108]. A comparative study of calciphylatic responses of various iron-tartrate compounds to prevent anemia in animals has been carried out [109]. Copper tartrate has shown in vitro to stimulate Luteinizing hormone.

There are also other numerous applications of compounds of tartaric acid in science and technology [97], for example, ferroelectric applications of sodium-potassium tartrate [100] and calcium tartrate [110], ferroelectric-ferroelastic applications of sodium ammonium tartrate [111] and dielectric applications of lithium thiallate tartrate [112]. Some tartrate compounds are used in military applications.
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Strontium tartrate is used in the tracer compound in ammunition units [113]. Manganese tartrate crystals being temperature sensitive can be used to sense and measure the temperature in terms of precise change in coloration [46]. A wax pencil is developed to sense the surface temperature of heated substance in terms of change in the coloration upon contact. The change in coloration of these crystals occurs at 410°C from pink to black. The coloration change is almost instantaneous and occurring within 1 to 2 seconds. Gvozdov and Erunov [114] have described this method. The effect of light on copper tartrate has been examined [44].

There are certain industrial applications of different tartrate compounds. Zinc tartrate with other compounds form a bright coating and protecting powder for metals [115]. Also, antimony tartrate is used in corrosion inhibitive composition for coolant systems [116]. Calcium tartrate crystals show many interesting properties such as ferroelectric, dielectric, optical and thermal properties [101].

Various important applications of different tartrate compounds have led the present author to grow lead-cadmium (Pb-Cd), lead-iron (Pb-Fe), and lead-cobalt (Pb-Co) levo tartrate crystals by the gel technique and characterize them by various techniques. Earlier, in the present author’s laboratory iron (II) tartrate, iron-nickel tartrate, iron-cobalt tartrate [43], manganese tartrate [92,117] and copper tartrate [44] crystals were grown and characterized. The characterization of the grown crystals is expected to provide detailed knowledge of mixed tartrate crystals and perhaps their new applications. As far as the knowledge of the present author is concerned no reports are available in the literature on the growth of mixed levo tartrate crystals of lead-cadmium, lead-iron and lead-cobalt.

The aim of the present author is to structurally study crystals by powder XRD, obtain the elemental composition by EDAX, identify the active functional groups by FTIR spectroscopy, study the magnetic properties by VSM, study dielectric properties, study the impedance characteristics, study the thermal stability by TGA and, finally, the kinetic and thermodynamic mechanism of dehydration of samples.
References


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