Preface

Crystallization is a multiparametric process involving the three classical steps of nucleation, growth and cessation of growth. Usually, the different steps of the growth process are discussed as if crystallization were a sequence of unconnected events. Actually, all steps are interdependent since the system in which crystallization occurs is in continuous evolution. As nucleation and growth proceed, the overall supersaturation of the parent phase decreases and nucleation and growth kinetics are decelerated. Accordingly, the system tends towards equilibrium and the thermodynamic factors take precedence over the kinetic factors. Unless the growth is ceased, new polymorphic modifications, habit changes, Ostwald ripening and phase transitions may occur.

Nucleation is the process of formation of the initial fragments of a new stable phase in an unstable or metastable parent phase. It occurs due to energy fluctuations around the increased mean value of the free energy induced by the supersaturation. To create a new phase, the system must overcome a certain energy barrier called activation free energy of germination or simply the free energy of formation. The formation of a new phase in an initial phase comprising of a large number of monomers (atoms, ions, molecules or molecular assemblies) begins when a few monomers stick together to yield small clusters called embryos. In the classical kinetic theory of the problem, nucleation is treated as the chain reaction of monomolecular addition to the clusters and ultimately reaching macroscopic dimensions. The growth of an embryo into macroscopic size is not guaranteed since there is equal chance for the molecules forming the cluster to disintegrate. From the classical nucleation theory one understands that if the embryo reaches a critical size, its spontaneous disintegration becomes thermodynamically impossible. Such a nucleus, called critical nucleus grows into a macroscopic crystal.

Nucleation, in a particular case is considered homogeneous when it occurs spontaneously in the bulk of the parent phase and heterogeneous when the nuclei are formed on impurity sites. Nucleation is termed as primary if it takes place in systems that do not contain the crystalline forms of the same material. Formation of nuclei on an already existing crystal is referred to as secondary nucleation.
There are different physicochemical factors that affect the free energy of formation. Supersaturation, temperature, pH, time, ionic strength, purity of chemicals, diffusion and convection are a few factors whose impacts are well explored. There are also a few parameters, the influence of which are poorly studied. This thesis is the report of a comprehensive exploration of both the theoretical and the experimental aspects of the nucleation kinetics of crystals under electric and magnetic fields. Also, the impact of fields on crystal morphology, lattice parameters and magnetic properties are presented. The thesis is divided into seven chapters.

The first chapter forms a presentation of the nucleation phenomenon. The classical expressions for the free energy of formation, critical radius, nucleation density and nucleation rate are discussed in the opening pages. Differentiation has been made between vapors, solution and melts. Techniques for the experimental determination of nucleation and nucleation rate are the topic of discussion in the next part. A brief description of the heterogeneous nucleation is given in the adjacent section. The chapter closes with a small narration of Ostwald ripening phenomenon, which usually affects the particle size distribution in a nucleation experiment.

The second and third chapters give up to date reviews of the impact of electric field and magnetic field respectively on nucleation, growth and orientation of crystals and crystal properties. Scientific observations drawn from a wide range of research papers published till date are consolidated here. Each chapter treats the theoretical and the experimental observations separately.

An extension of the existing theories developed to study the influence of electric field on the nucleation of crystals in supersaturated solution shapes the opening pages of Chapter 4. Special care has been taken to derive equations, which are compatible with the experimental set ups designed in the experimental sections described in the proceeding chapters. The theory enables one to predict the electric field impact, provided that the dielectric constants of the parent and daughter phases are known. The chapter closes with the report of the theory formulated to understand the extent of magnetic field influence on nucleation kinetics of crystals in solutions. The thermodynamic analysis of the problem presented here reveals that the nature of magnetic influence will depend on the permeabilities of the initial and final phases. Furthermore, it is seen that the influence of the fields will be stronger in systems that
produce nucleation at lower supersaturation values. The monomer size of the daughter phase is another factor that affects the strength of the influence.

Details of the experiments conducted to investigate the effect of electric fields on the nucleation of crystals in sitting drops and in bulk solution are reported in Chapter 5. It opens with the description of the design and fabrication of special kinds of crystallization vessels that matches the theoretical model developed in Chapter 4. Next part of the chapter brings the effect of electric fields on the nucleation of three inorganic materials NaCl, KCl and KDP and a metal-organic compound crystal- bis-thiourea zinc chloride (Zn [CS (NH$_2$)$_2$]$_2$ Cl$_2$). Nucleation is experimented in sitting drops exposed to electric fields of strength up to 7.5 x 10$^5$ V/m. Then it presents the design of the experimental set up constructed to study the impact of electric field on the nucleation kinetics in bulk solution. Finally, nucleation kinetics of bis-thiourea zinc chloride in bulk solution is reported.

The impact of magnetic field on the nucleation and crystal formation of three materials, calcium tartrate and praseodymium tartrate in hydro silica gel, and calcium carbonate in solution has been examined and the details are disclosed in Chapter 6. The first and third materials belong to the diamagnetic category and the second to the paramagnetic group. Weak magnetic fields created by permanent ferrite magnets were used to study the crystal formation in gel column over long duration. Crystal formation at the free surface of the gel was studied under fields of strength up to 3 T in shorter duration. Optical microscopy and scanning electron microscopy were employed to study the morphology and surface texture of the crystals. Particle size analysis of the calcium carbonate crystals was done on Microtrac- X100 laser particle size analyzer. Illuminating conclusions pertaining to the impact of magnetic exposure on the number density, size and even morphology of calcium carbonate crystals are drawn from the particle size distribution yielded. Also, the changes observed in the XRD and IR spectra, magnetic properties and growth habit of the samples grown under magnetic fields are discussed. A comparison between the theoretical prediction and the experimental results obtained for each material is illustrated at appropriate junctures.

The conclusions drawn from the theoretical and experimental studies are consolidated in Chapter 7. The thesis ends with a brief mention of the scope for further research in the topic.
The research work presented in this thesis has been either published in or communicated to refereed journals. Furthermore, some portions of the work are presented at national seminars.

**List of Papers Published/Communicated**

1. Thermodynamics of Crystal Nucleation in an External Electric Field
2. The Influence of Electric Field on the Nucleation of NaCl crystals
3. Thermodynamics of Crystal Nucleation in Drops, Hanging or Sitting in an External Electric Field
4. Influence of magnetic field on the growth and properties of calcium tartrate crystals
   Journal of Magnetism and Magnetic Materials (accepted).
5. Effect of Magnetic Field on the Gel-assisted Growth of Praseodymium Tartrate Crystals
   J. Crystal Growth (communicated).
6. Effect of Static Magnetic Field on the Particle Size Distribution and Morphology of Calcium Carbonate Crystals
   Journal of Magnetism and Magnetic Materials (communicated).

**Seminar Presentations**

1. Temperature Controlled Magnetic Field Set up for the Study of Crystal Nucleation
2. Effect of Electric Field on Nucleation

3. Impact of Magnetic Field on the Growth and Properties of Praseodymium Tartrate Crystals
   National Seminar on Crystal Growth, February 2003, Crystal Growth center, Anna University, Chennai (accepted for presentation).