1. INTRODUCTION

In this chapter we present some background information related to crystals and crystal growth along with introducing the actual research work done by the author.

1.1 About Crystals

Crystals have always been recognized as being distinct from other forms of matter for as far back as history has been recorded. The word 'crystal' is derived probably from the Greek word meaning 'ice'. We are all able to recognize crystals when we see them, such as salt and sugar, but it is less widely realized that most solid material can occur in the form of crystals, even if they are tiny. Crystals are found throughout the natural world as the stable form of metals, organic and inorganic chemicals, natural and synthetic products and in biological organisms. Even bone has something of a crystalline content to it.

The atomic aggregates are normally classified into three states of matter, viz., the solid state, the liquid state and the gaseous state. The matter in the solid state can be classified into crystalline and amorphous. A solid material in which the constituent atoms arrange themselves in an ordered periodic pattern is called crystalline and a solid material which does not have such a periodic arrangement is called amorphous.

Imperfections in the regularity of arrays are found in the real crystals. The imperfections quite commonly found are disorders, dislocations, twinning, etc. However, in a single crystal, we can approximate the order to be perfect because a substance is crystalline if it has regular arrays of atoms extending over a millionth of an inch. If the component crystals in a piece of matter are that large, then each crystal contains a million atoms in orderly array still not visible through a microscope.
1.2 Natural and Artificial Crystals

The beauty of large single crystals is arresting. The flatness of their faces, the sharpness of their angles, the purity of their colours will give you a deep satisfaction. The man lived in the early days was also arrested by the beauty and symmetry of the crystals. But in those days crystals were appreciated mainly for their ornamental values. Diamonds, emeralds, rubies and sapphires have been of great value from early days. The size of crystals found in nature varies between several kilos to microscopic level.

Attempts to make artificial materials to replace natural ones have been going on for a very long time. In 1902 Verneuil, a Frenchman, invented a process for making synthetic rubies and sapphires. These were used to replace glass in certain scientific instruments. The natural gems have too many flaws, the man made ones are better. Natural rock salt was used in instruments for studying infrared radiation. These radiations are not transmitted through glass and so lenses cannot be used. So clear rock salt is used in infrared cameras. Large and perfect rock salt crystals for this purpose can now be synthetically prepared.

1.3 Importance of Crystals

Crystal studies originated with the structural investigation of natural crystals. Later, due to the development of X-ray diffraction, internal arrangement of atoms in a crystal was explored. This led to the study of laboratory grown crystals with desired physical properties.

Crystals are the unacknowledged pillars of modern technology, which is very much dependent upon materials/crystals such as semiconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers and nonlinear optic, acoustooptic, piezoelectric, photosensitive materials and crystalline films for microelectronics and computer industries. All this involves research in crystal growth.
Truly stupendous sums have been spent on the growth of pure and perfect crystals of silicon, upon which most of the present boom in the information technology depends. The list of new and interesting technologically important crystals grows ever longer. We can expect to see increasing use made of new crystals in computers, communications and in other high technology areas. GaAs crystals replace silicon in the semiconductor industries. Hundreds of pages of information can now be stored holographically within a single crystal, and in communications, crystals are currently being considered to their optical changes when sound waves are passed through them.

Days are not far off for the telephone companies to tear out their cables replacing with optical fibres. Regarding the optical communication, most of tomorrow's interesting such as being somewhere, being somebody and being at someone's time will work by manipulating light and not electricity. It is worth switching to photon, because it travels much faster than electron, has no mass and can be made to pass through each other unperturbed. The above mentioned technological feats are possible only because of the constant and tireless efforts of crystal growers who continue their search for newer and better materials.

The increasing demand for storage and processing of data has encouraged interest in photo-refractive crystals. The interaction of laser light with crystals such as bismuth silicate and barium titanate produces a small change in refractive index. The phenomenon, the photo-refractive effect, is being exploited for recording holograms and development of phase-conjugate optics.

The most exciting and at the same time widely anticipated contribution to molecular biology made by crystallographers in the recent years has been the direct visualization at atomic resolution of nucleic acid and variety of proteins with which it interacts. Indeed, it appears likely that sound structural basis is now in the making of interpretation of protein-nucleic acid interactions at highest level of details. From this will emerge an understanding in molecular biological and classical chemical terms of the process by which genetic events are initiated, mediated and ultimately regulated.
At the same time the multitude of the essential cellular processes involving the interplay of these macromolecules can begin to interpret in a structurally consistent and rational manner.

Artificial crystals are grown everyday and now we are more concerned to discover new materials for the purpose of industrial and academic uses. At present, industries, science and technology hardly make any progress without the development of new materials of enhanced performance. Due to the increased need of crystals in solid state devices, scientists' interests have turned from pure crystals to mixed and impurity added (doped) crystals (controlled mixing and controlled doping). Moreover, crystal growth is an expanding field in materials science, which is identified as a thrust area of research.

1.4 Crystal Growth

The orderliness of the atomic arrangement in a crystal is certainly its most important feature. But another feature is the fact that a crystal does not suddenly spring into being; it grows into being. It has long been appreciated that advances in solid state science depend critically on the availability of single crystal specimens. As a result, an enormous amount of labour and care has been lavished on the development of growth techniques. In terms of crystal size, purity and perfection the achievement of the modern crystal grower are remarkable indeed, and vast sections of industry now depend on his products. So do the research workers whose preoccupation is with new materials, no matter whether these are under investigation for practical reasons or because a knowledge of their properties might throw new light on our understanding of solids in general.

In one way or another, a very large number of new materials have already been grown as single crystals in recent years, some with relative ease and others only after long and painstaking research. Nevertheless, there are still many substances, which have defied the whole array of modern techniques and which, accordingly, have never been seen in single crystal form. Others, though grown by conventional methods, have
never been obtained in the required size or degree of perfection. All these constitute a challenge and an opportunity not only for the professional crystal grower but also for a talented amateur. New and unusual methods of growing crystals are therefore of wide interest.

If the crystal is in a dynamic equilibrium with its parent phase the free energy is at a minimum and no growth will occur. For growth to occur this equilibrium must be disturbed by a change of the correct sign in temperature, pressure, chemical potential (e.g. saturation), electrochemical potential (e.g. electrolysis), or strain. The system may then release energy to its surrounding to compensate for the decrease in entropy occasioned by the ordering of atoms in the crystal and evolution of heat of crystallization. In a well-designed growth process just one of these parameters is held minimally away from its equilibrium value to provide a driving force for growth.

Growth of single crystal ranges from a small, inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. Crystal growth needs the careful control of a phase change. Depending on the nature of the starting material, there are different methods to grow crystals. Three main categories of crystal growth may be defined.

Growth from the solid : \( S \rightarrow S \) processes involving solid-solid phase transitions;

Growth from the melt : \( L \rightarrow S \) processes involving liquid-solid phase transitions;

Growth from the vapour : \( V \rightarrow S \) processes involving vapour-solid phase transitions;

A fourth main category may be defined which is strictly included in the above definitions:
Solution growth: growth of a solute from an impure melt.

This is done primarily because solution growth is such a large and important category and because solution growth methods differ from methods used for pure melt growth.

So we have four main categories of crystal growth techniques: Solid growth, vapour growth, melt growth and solution growth.

Gel growth is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. The following shows how these main categories break into subsfamilies of related growth techniques.

**Crystal growth techniques**

- Melt growth
- Solution growth
- Solid state growth
- Vapour phase growth

**Melt growth**

- Normal freezing
  - Skull melting
  - Directional freezing
  - Cooled seed

- Zone melting
  - Float zone melting

- Crystal pulling
  - Pedestal pulling
  - Shape controlled crystal pulling
Automated crystal pulling
Liquid encapsulation pulling
- Flame fusion
  - Plasma heating

Solution growth
- Gel growth
- Organic solution growth
- Electrocrystallization
- Flux growth
  - Accelerated crucible growth
- Aqueous solution growth
  - Hydrothermal growth
- Molten metal growth
  - Liquid phase epitaxy
  - Vapour liquid solid growth

Solid state growth
- Polymorphic phase transitions
- Strain anneal
- Zone heating
- Sintering

Vapour phase growth
- Sublimation
- Gas transport processes
- Gas phase reaction

For bulk growth of high quality single crystal, material seeded melt growth (e.g. crystal pulling or float zone melting) is undoubtedly the best method available for congruently melting materials. When a material is wanted in thin film form with
accurately controlled doping, composition and quality on available substrate material as in the semiconductor and photonics industries, vapour deposition, especially chemical vapour deposition (CVD) or molecular beam epitaxy (MBE), is an appropriate method, although sometimes solution growth is preferred. In other cases solution growth is the next best choice - using seed crystal if possible. This is a particularly useful method of obtaining small crystals of new materials for scientific research. Sometimes, as with biological crystal growth and gel growth, the conditions cannot readily be chosen - they are fixed by the system.

There are very large number of published articles, books and proceedings of schools and conferences on various aspects of crystal growth theory and practice. Some of the general books to read are by: Buckley [1], Gilman (Ed.) [2], Laudise [3], Hartman [4], Pamplin (Ed.) [5], Holden and Morrison [6], Brice [7], Mullin [8], Ramasamy and Santhana Raghavan [9], Byrappa et al (Ed.) [10], etc.

In the present study, we have used gel method for the growth of single crystals. Some details of gel methods along with a brief note on other crystal growth methods are presented in Chapter 3.

1.5 Present Study

In the present research work (a scientific research), it was aimed to grow and investigate the growth conditions of pure and impurity (Sr^{2+}) added calcium tartrate tetrahydrate single crystals (sample crystals) of considerable size, high transparency and good morphological perfection.

Density was measured by using flotation technique and the entry of the impurity into the crystal was confirmed by atomic absorption spectroscopy (AAS).

X-ray diffraction data were collected from powder samples of crystals using an automated X-ray diffractometer. The reflections were indexed and the lattice parameters were determined.
Mean Debye-Waller factors were determined from the X-ray powder diffraction intensity data by the Wilson plot method. Other thermal parameters like mean-square amplitude of vibration, Debye temperature and Debye frequency were determined using the mean Debye-Waller factor.

The a.c. and d.c. electrical conductivities and dielectric loss were determined from impedance measurements at different frequencies ($10^2$-$10^4$ Hz) for various temperatures ranging from room temperature to 75°C. Activation energies were also determined.

Microhardness measurements were carried out on the pure and impurity added (1.6 mole% only) crystal using Leitz microhardness tester. The Vicker's microhardness number ($H_v$) was determined. The work hardening coefficients were determined in order to find whether the crystals belong to hard or soft category.

FTIR spectral studies were carried out on all the grown crystals. The important groups of atoms associated with the sample crystals were identified and their respective band assignments were done.

Thermogravimetric analysis (TGA) was done on the grown crystals. The decomposition stages were determined.

A report of this research work is presented in this thesis.

Chapter 2 gives a brief review of various studies made on calcium tartrate tetrahydrate crystals in the near past.

A brief description of the gel method and other crystal growth methods together with providing the details of methods adopted in the present work for the growth of sample crystals are given in Chapter 3. The results obtained in our crystal growth experiment are discussed.
In Chapter 4 we present the results obtained in the density measurements and AAS studies on the grown crystals. The results obtained are discussed in the last section of the chapter.

X-ray diffraction data collection on powdered samples of all the crystals grown along with the determination of lattice parameters and checking for lattice distortion are dealt with in Chapter 5.

Chapter 6 deals with the determination of thermal parameters like Debye-Waller factor, Debye temperature, mean square amplitude of vibration and Debye frequency from the X-ray powder diffraction data.

The results obtained in our electrical conductivity and dielectric loss measurements are reported and discussed in chapter 7. A brief description of the method followed in the present study is also given. The results are discussed in the last section.

In chapter 8, we present the results obtained on microhardness measurements, FTIR spectral studies and thermogravimetric analysis. The last section of this chapter provides the discussion on the results obtained.

Chapter 9 contains the summary and conclusions derived out of the present study and chapter 10 contains the scope for future work in the same area of research.

The literatures cited in each chapter are listed in the ‘References’ section provided at the end of each chapter. Finally in the ‘Appendixes’ section a brief resume of the candidate together with a list of publications by the candidate is added.
References


