Chapter I

INTRODUCTION
1.1 HISTORICAL DEVELOPMENT

The beautiful world of crystals was admired by man from time immemorial. The gems and crystals delivered by mother earth have always attracted mankind. Man has learned the art of cutting, cleaving and polishing of gemstones to enhance the sparkle which arise from their high refractive index and dispersion. The significance of their beauty for the development of scientific knowledge has only begun to be realized however [Holden and Singer, 1960].

Today crystals play a very important part in electronic and photonic industries, such as production of high efficiency photovoltaic cells and fabrication of bright long-lifetime emitting diodes.

1.2 SIGNIFICANCE OF CRYSTAL GROWTH

Crystal growth is a multidisciplinary field which demands collaboration of chemical and process engineers, electrical and mechanical engineers, instrumentation engineers, material scientists, numerical simulation specialists, physicists and crystallographers. The present day demand is for large and high quality ferro electric, piezo electric, oxide single crystals with minimum defects and inhomogeneities. The important goal of the science and technology of crystal growth, namely the improvement of the microscopic and macroscopic homogeneity, is a necessity for any application.
1.3 APPLICATION

1.3.1 Semiconductor crystals

The enormous need for single crystals in semiconductor industry is not only to grow elemental semiconductors but also the new breed of compound semiconductors like III - V and II - VI semiconductors.

1.3.2 Oxide crystals

Today, parts fabricated from oxide single crystals are used as active components in laser systems (Ti: Al₂O₃, Cr: Al₂O₃).

1.3.3 Alkali halide crystals

The emergence of NaI : Tl, the scintillation crystals have found wide applications in radiation detection. The halogenide scintillators are among the most widespread type of scintillation materials and they are classified under two broad groups: 1. Alkali halide scintillators like NaI : Tl, CsI : Na, CsI : Tl, LiF : Eu and 2 Fluoperovskites such as LiBaF₃, KMgF₃, KCaF₃, CsCaBr₃, CsSrBr₃, RbMgF₃.

1.3.4 Nonlinear optical crystals

Nonlinear optical (NLO) crystals are very important for laser frequency conversion. KDP is a suitable crystal for higher harmonic
generation of huge laser systems and for fusion experiments because it can be grown to larger sizes and it has a high laser damage threshold.

Various kinds of organic NLO crystals have been developed in these twenty years because of the possibility of extremely high optical nonlinearity. L-Arginine phosphate, 4-dimethylamino-N-methyl-4-stilbazolium tosylate and urea are some examples of organic nonlinear materials.

1.3.5 Quartz crystal

Quartz crystals due to the piezoelectric property, optical rotation and high transparency over a wide range of wavelengths into UV, visible and IR regions of the spectrum are widely used in modern electronics and in the field of optical instrumentation. Also many varieties of coloured quartz are also available which are used in jewellery.

1.4 TECHNIQUES OF CRYSTAL GROWTH

Various techniques of growth of single crystals have been developed over the years to meet the needs of basic research and applications. Basic methods have been modified and refined to enhance their applicability to specific materials or classes of materials.
Crystal growth still remains an art. There is an unbridged gap between the theory and experiment, primarily because the overall crystal growth process is very complex, as it is influenced by numerous interdependent parameters, particularly when controlled chemical composition and homogeneity, crystalline perfection, orientation and size are considered.

Growth of crystals 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 methods are generally classified into three categories – growth from the melt, growth from solution and growth from the vapour phase [Brice, 1973].

1.4.1 Growth from the melt

In principle, all materials can be grown in a single crystal form from the melt, provided they melt congruently, they do not decompose before melting, and they do not undergo a phase transformation between the melting point and room temperature (phase transformations are generally accompanied by volume changes leading to excessive strains, defects or polycrystallinity). Melt growth can be achieved by a large variety of techniques depending
on the specific properties of the material and requirement on size and shape.

As a general procedure a crystal seed of the same material is used (heterogeneous nucleation) although a seed of another material can be employed or the use of the seed can be eliminated (homogeneous nucleation).

1.4.1.1 Czochralski method: Czochralski-type system is shown in figure 1.1. In this method [Brice, 1973] a crucible is used to contain the melt. A seed held by a rod is dipped into the melt and after equilibrium, the seed is slowly pulled by the rod while the rod is rotated at an appropriate rate. In many cases the crucible is also rotated during growth. Rotations of seed and crucible are employed to optimise compositional and thermal homogenization of the melt and to control the geometric configuration of the crystal.

The Czochralski method is very widely used. About 75% of all silicon used in the electronic industry is grown by this method.

This method has the advantages that the growth from a free surface accommodates the volume expansion associated with solidification of materials. By this method large single crystals can be

Figure 1.1: Czochralski-type system for crystal growth
obtained at high speeds (several inches per hour in the case of Si). The diameter of the crystals can be varied at will by adjusting the thermal parameters in conjunction with the rate of growth. High crystalline perfection can also be achieved. The method lends itself to convenient chemical composition control (doping) by using the appropriate melt composition. Finally during Czochralski growth the desired ambient atmosphere can be used, controlled and changed.

However this method does not support readily to the growth of materials whose vapour pressure or that of one of their constituents is high at the melting point. Moreover there are engineering problems in accommodating rotation and pulling of the crystal, and with the thermal configuration requirements for maintaining thermodynamic equilibrium between the vapour and the melt.

The requirement for a crucible presents the obvious hazard of contaminating the melt. Czochralski method is not easily adaptable to continuous growth. Although cold-crucible techniques and continuous feeding of the melt are possible, they present major engineering problems, at least for the growth of materials with high melting points.
1.4.1.2 Normal freezing and zone melting: In the normal freezing method the charge is contained in a closed container which can be mounted horizontally or vertically. If no seed is used, the entire charge is melted; solidification is initiated and the solid-melt interface is advanced horizontally by moving the container through a furnace with appropriate thermal gradients or by moving the furnace past the container. Single crystals, particularly if a specific orientation is desired, cannot be predictably obtained by normal freezing. Accordingly, a seed is commonly used at one end of the container. Single crystals with a preferred orientation are obtained by Bridgman method [Brice, 1973]. Bridgman-type apparatus is shown in figure 1.2. In this technique the material to be grown is taken in a vertical cylindrical container, tapered conically with a point bottom and made to melt using a furnace. The container is lowered slowly from the hot zone of the furnace into the cold zone. Crystallization begins in the tip and continues usually by growth from the first formed nucleus.

Normal freezing methods are extensively used for growing single crystals of materials with volatile constituents.

In zone melting a molten zone is established at one end of the charge (or between the seed and the charge, if a seed is used) and is
Figure 1.2: Bridgman-type apparatus for crystal growth
advanced by moving either the container or the furnace. The zone-melting configuration is shown in figure 1.3.

The distinct difference between normal freezing and zone melting is with regard to the segregation of impurities (doping). In principle an effective distribution coefficient of one can be achieved in zone melting due to the relatively small volume of the melt, whereas segregation in normal freezing is controlled by diffusion convective mass transport of the impurities in the melt. Thus, the distribution of a given impurity in the two cases are significantly different. It is apparent that a homogeneous distribution of impurities can be achieved by a zone melting in a significant portion of the crystal. Zone melting or zone refining was developed for the purification of semiconductors. It is now widely applied to many class of materials including organic materials.

Directional solidification methods are characterized by their simplicity and versatility. In these methods it is easy to control the vapour pressure of volatile constituents; alternatively, growth can be carried out in evacuated and sealed containers. Shape and size of crystals can be conveniently controlled. Furthermore, growth can be carried out under stabilising thermal gradients which minimize convective interference in growth and segregation.
Figure 1.3: Zone-melting configuration for crystal growth
However the confining configuration in these methods present considerable limitations. When volume expansion is associated with solidification, pressure can be exerted on the growing crystal leading to high densities of lattice defects.

Float-zoning is essentially zone melting in a vertical configuration without a container. The zone is sustained by surface tension forces. This method is suitable for materials with high surface tension and low density. Float-zoning is extensively used for the growth of Si single crystals with a very low oxygen concentration having a diameter of several inches. It is also used for high purity crystals of metals.

The unique advantage of float-zoning is the elimination of the melt container which invariably is the source of contamination.

However float-zoning is not suitable for the growth of materials with high vapor pressure or of materials with volatile constituents.

1.4.2 Growth from solution

This method of crystal growth is more widely used as compared to the growth from the melt or from the vapor phase. In this method, a saturated solution of the material in an appropriate solvent is used,
from which growth takes place after the solution is supersaturated by evaporating the solvent (isothermal methods) or by lowering the solution temperature (non-isothermal methods). There are numerous general and specific methods of solution growth. They are usually classified according to the type of solvent used. Some of the solution growth methods are aqueous-solution, molten-salt (flux), metallic-solution and hydrothermal growth.

Solution growth is simple and inexpensive. Materials which melt incongruently or decompose before melting or undergo a phase transformation between the melting point and room temperature can be grown by solution method. Growth from solution, however, is used more broadly because, when compared with growth from the melt, it requires lower temperature and can lead to lower density of lattice defects. Growth from the aqueous solution can be visually inspected; in fact it has been extensively used for studying growth parameters.

The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the case of solvent inclusion into the growing crystal.
'Flux growth', the most commonly used term for crystal growth from high temperature solutions (HTS), is a method which allows the growth of single crystals from a wide range of materials [Elwell and Scheel, 1975]. The flux growth process is analogous to crystal growth from solution, but the solvent solidifies before reaching room temperature. In this the crystals are grown below the melting temperature. Flux growth is useful for synthesis of compounds with high melting point. Flux is used as a molten solvent to speed crystallization up at lower pressure and temperature.

The largest single crystal formed in nature (beryl crystal) and some of larger crystals created by man (quartz) are both of hydrothermal growth. Minerals formed in the postmagnetic and metasomatic stages in the presence of water at elevated temperatures and pressures are said to be of hydrothermal origin. In hydrothermal growth aqueous solvents or mineralizers under high pressure and high temperature are used to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions. In hydrothermal growth, the dissolution is carried out at the lower hotter zone (nutrient zone) and crystallization is carried out at the upper cooler zone (growth zone).
1.4.3 Growth from the vapour phase

Gases in general can be obtained at higher levels of purity than liquids, and higher purity conditions can usually be maintained during gaseous processes. Accordingly, vapour phase growth can readily lead to high purity materials. Bulk as well as thin layers are prepared from the vapour phase.

Two main types of vapour phase process can be distinguished. The first involves direct transport of material by evaporation or sublimation from a hot source zone to a cool growth region. The second method involves chemical transport in which material is transported as a chemical compound which decomposes in the growth area.

Growth from the vapour phase can be obtained without involving chemical reactions such as sublimation-condensation methods and sputtering of elemental materials. Sublimation-condensation methods and sputtering can be used for the formation of layers through irreversible reactions. However, more commonly the growth through chemical reactions (irreversible or reversible) is carried out in apparatus permitting controlled flow or transfer of the reacting species over the seed material.
Very high purity materials are obtained by irreversible reaction process. The thickness and the doping level of the layers is readily controlled. Single crystals and epitaxial layers of high chemical purity and crystalline perfection can be obtained from the vapour phase by reversible reactions. The process can be recycled.

However growth by this method is slow and thus not suitable for bulk single crystals.

1.4.4 Gel growth

Gel technique is a simple method of growing single crystals under controlled growth and at room temperature. The principles used in this crystal growth technique are simple. Solutions of two suitable compounds which give rise to the required insoluble crystalline substance by more chemical reaction between them are allowed to diffuse into the gel medium and chemically react as follows:

\[ AX + BY \rightarrow AB + XY \]

where AX and BY are the solutions of the two compounds which after reactions give rise to the insoluble or sparingly soluble substance AB and also the waste product XY which is highly soluble in water.
The growth of single crystals in gel is a self purifying process, free from thermal strains which is common in crystals grown from the melt [Henisch, 1970].

1.5 NON LINEAR OPTICS

When an intense beam of light passes through a dielectric medium, the electrons and atoms interact with the electromagnetic fields in the wave. The impact of the forces exerted by the fields on the charged particles is a displacement of the valence electrons from their original orbits. This agitation generates electric dipoles whose macroscopic appearance is the polarization. For a small field strength, this polarization is proportional to the electric field. This is known as linear optical effect. In the nonlinear case, the reradiation comes from dipoles whose amplitude does not faithfully reproduce the sinusoidal electric field that generates them. Therefore the distorted reradiated wave contains different frequencies from that of the original wave.

Nonlinear optics is a very useful technology because it extends the usefulness of lasers by increasing the number of wavelengths available. Wavelengths both longer and shorter than the original can be produced by nonlinear optics.
1.5.1 Nonlinear optical materials

Nonlinear optical materials are expected to be active elements for optical communication, optical electronics or electro-optic modulation, frequency mixing or frequency conversion, second harmonic generation etc.

1.5.1.1 Inorganic materials: In the initial stages the materials analysed for nonlinear optical applications had always been inorganic. Many inorganic crystals were well studied in terms of their physical properties. Since these materials are mostly ionically bonded, it is always easy to synthesize these materials. Inorganic materials have high melting point, mechanical strength and high degree of chemical inertness. High temperature oxide materials were well studied for diverse applications like piezoelectricity, ferroelectricity, pyroelectricity and electro-optics. Some of the oxide materials showed nonlinear optical property and some of the most useful crystals are LiNbO$_3$, KNbO$_3$, potassium dihydrogen phosphate (KDP) and its analogues, potassium titanyl phosphate and its analogues, and $\beta$-barium borate. Most of the commercial frequency doublers used presently are all made of these inorganic materials.

1.5.1.2 Organic materials: Organic compounds are often formed by weak van der Waals and hydrogen bonds and hence posses high
degree of delocalization. Thus they are expected to be optically more nonlinear than inorganic compounds. Some of the advantages of organic materials include flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high damage resistance etc [Williams, 1983; Chemla and Zyss, 1987; Bailey et al, 1993]. The prototype organic nonlinear optical material contains one or more delocalised bonds, typically a ring structure like benzene. When substituted with donor and acceptor at the para position (e.g. p-nitro aniline), they have large induced dipole moments under the influence of electromagnetic fields. However, such structures, when packed as crystals tend to be mostly centrosymmetric, thus leading to vanishing dipole moment. A suitable addition at another site as in the case of 3-methyl-4-nitroaniline, can ensure a macroscopically non-vanishing dipole moment for the donor-acceptor substituted systems.

Organic crystals hold promise because of large variety of such materials and the potential to synthesize molecules according to some design principles. As a result there have been efforts at developing such materials for application in nonlinear optics. The compounds which have been reported are nitroaniline derivatives such as 2-methyl-4-nitroaniline (MNA) [Levine et al, 1979], N-(4-nitrophenyl)-(1)-prolinol (NPP) [Zyss et al, 1984], N-(dimethylamino)-5-
(nitrophenyl) acetamide (DAN) [Kerkoc et al, 1989], -2-(α-
methylbenzylamino)-5-nitropyridine (MBANP) [Tweig et al, 1982],
aminobenzophenone (ABP) [Frazier and Cockerham, 1987], bis-
benzylidinecycloalkanones derivatives [Jun Kawamata, 1992], methyl-
p-hydroxibenzoate (MHB) [Terephaganon, 1971], Urea, N-methyl
urea (NMU), carbohydrazono-pyrazole derivative [Masanori et al,
1992], 3-methyl-4-methoxy-4′-nitrostibene (MMONS) [Wilson et al,
1989], substituted thienyl chalcone [Goto et al, 1991], substituted
chalcones [Fichou et al, 1988; Kitaoka et al, 1990; Tokiko et al,
1998].

Among many organic compounds reported for their second
harmonic generation, chalcone derivatives are noticeable materials
for their excellent blue light transmittance and good crystallizability.

Organic NLO materials are inherently poor in mechanical
hardness, and have low melting points and poor chemical inertness.
Owing to high polar nature of the molecules they often tend to
crystallize as long needles or thin platelets.

1.5.1.3 Semiorganic materials: The inherent limitations on the
maximum attainable nonlinearity in inorganic materials and the
moderate success in growing device-grade organic single crystals
have made scientists adopt newer strategies. The obvious one was to develop hybrid inorganic-organic materials with little trade-off in their respective advantages. This new class of materials has come to be known as semiorganics [Newman, 1990]. One approach to high-efficiency, optical-quality organic based NLO materials in this class is to form compounds in which a polarizable organic molecule is stoichiometrically bonded to an inorganic host. Some of semiorganic NLO materials are L-Arginine phosphate monohydrate (LAP) and its deuterated analogue (d LAP) [Eimerl et al, 1989; Sasaki et al, 1989; Yokatani et al, 1989]. Zinc(tris)thiourea sulphate (ZTS), Bis(thiourea) cadmium chloride (BTCC), triallyl thiourea cadmium chloride (ATCC), triallyl thiourea mercury bromide (ATMB), thiosemicarbazide cadmium bromide etc.

1.6. PRESENT WORK

The present work is, mainly concentrated on the growth of chalcone derivative crystals and their characterization.

Chalcone and several chalcone derivative compounds were synthesized by Claisen-Schmidt condensation reaction method. This is the reaction of acetophenone/substituted acetophenone with benzaldehyde/substituted benzaldehyde in the presence of alkali. The synthesized compounds were recrystalized several times in ethyl
alcohol. The molecular structure or the compounds were confirmed from UV and IR spectra. The thermal stability and melting points of the samples were studied by using DSC. It was found that all synthesized compounds were stable. The solubility of the compounds were studied in different organic solvents like ethyl alcohol, methanol, acetone, N,N-dimethylformamide (DMF), xylene and benzene at different temperatures. Most of the compounds were sparingly soluble in ethyl alcohol, methanol and highly soluble in other solvents. Samples recrystallized in different solvents were grown into single crystals. For the compounds insoluble in water, organic solvents were used for the growth of crystals.

The crystals of the compounds 1-(4-methoxyphenyl)-3-(phenyl)-2-propen-1-one and 1-(4-methoxyphenyl)-3-(4-methoxyphenyl)-2-propen-1-one were grown using ethyl alcohol, methanol, acetone, xylene, benzene and N,N-dimethylformamide as solvents by slow evaporation technique, and crystals of different optical quality and size were obtained. Crystals grown in acetone were found to be more transparent and of larger size than crystals grown in other solvents.

The structural analysis of the crystal (1-(4-methoxyphenyl)-3(phenyl)-2-propen-1-one) was made by X-ray diffraction analysis. A
small crystal of good optical quality was chosen for the purpose. The space group of the crystal was found to be Pbca.

Mechanical strength of the crystal was studied by measuring its microhardness. Vickers microhardness test was used for the purpose.

The dielectric property of the crystals of a single compound grown in different solvents like acetone, benzene and ethylalcohol were studied using LCR bridge.