

Chapter – 1

Introduction

1. INTRODUCTION

The actual investigation carried out by the author is introduced here in this Chapter. Also we provide some background information related to the topic of research.

1.1. Crystalline State

Solid materials can be broadly classified into three categories: crystalline, amorphous and quasi crystalline. The crystalline state differs from the amorphous state in a regular arrangement of the constituent molecules or ions into some fixed and rigid pattern known as a lattice. This symmetry and tight packing of molecules result in the stability and hardness, high refractive index and related effects on light which makes it an interesting material in Materials Science and Engineering. In quasi-crystalline state the atoms are in ordered arrays, but the patterns they assume are subtle and do not recur at regular intervals. Such patterns are called quasi-periodic.

Normally in single crystals the periodicity extends through the material and it is free from inner boundaries. Crystals are subdivided into macro, micro and nanocrystals. Macro crystals are ordered crystals of mm ($\approx 10^{-3}$ m and above) size. They are visible (bulk single) crystals. Micro crystals are microscopically small crystals. Nanocrystals are crystals of dimensions $\approx 10^{-7}$ m and below.

If a crystal is having inner boundaries along with external boundary it is called polycrystalline. It is equivalent to the combination of a number of single crystals attached together at some point. If only two crystals are attached together it is called twinned, if more crystals are together it is called multiplex. In general, these are said to be polycrystalline. Figure 1 illustrates the classification of crystalline materials.

Crystals can be considered as regular polyhedral form bounded by smooth surfaces, which is assumed by a chemical compound under the action of its inner-atomic forces, when passing from the state of a liquid or gas to that of a solid under suitable conditions. In the case of crystalline substance the melting point is very sharp and they are compressible and rigid.

Real crystals often exhibit a variety of imperfections in the regularity of arrays, viz. dislocation, twinning and other kinds of defects. But the specimen under study should be perfect and three dimensional. So, for scientific research purposes, the researchers will grow crystals in the laboratory to their own taste.

1.2. Importance of Crystals

Crystals have been admired by man from ancient times because of their beauty. Crystallization of salt is mentioned in a Chinese reprint of 2700 BC. Crystals have fascinated men and women for many thousands of years. Naturally occurring hard gem stone crystals were priced along with gold in antiquity. The scientific approach to crystal growth was born during early 17th century when Kepler (1611) correlated the morphology and structure, followed by Nicolous Steno who explained the origin of

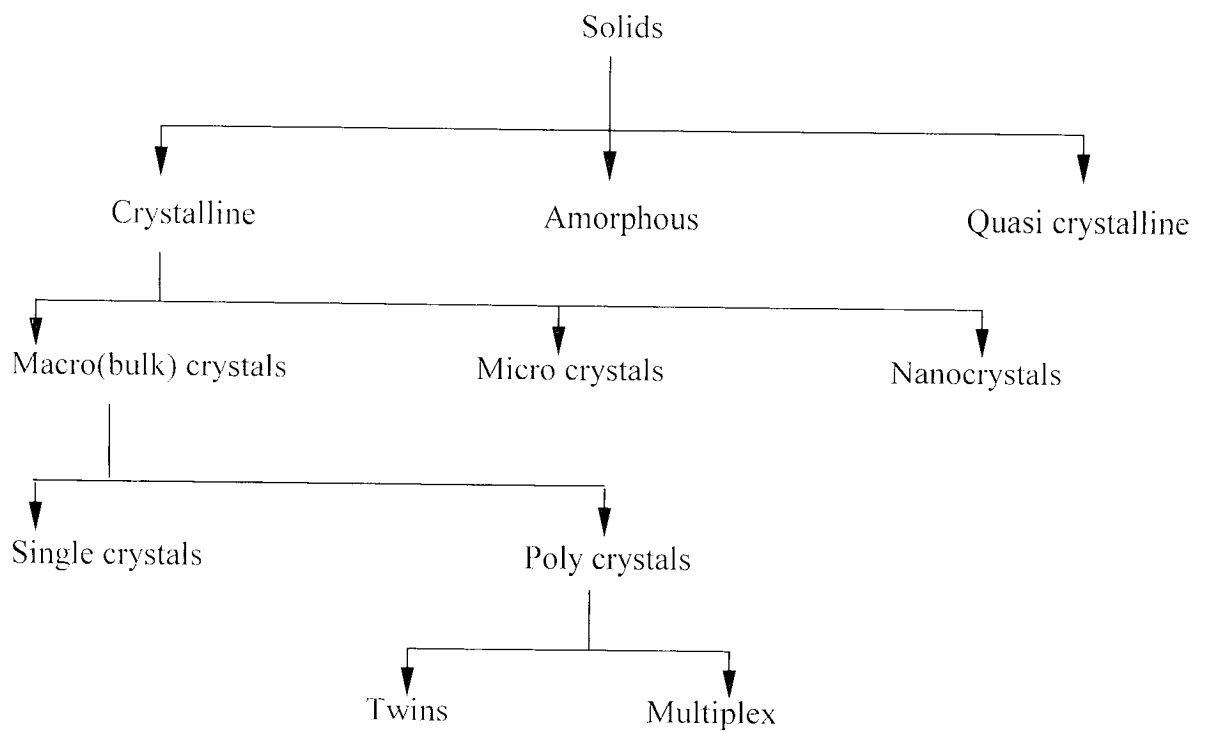


Figure 1: Classification of crystalline materials

a variety of external forms exhibited by natural quartz crystals in terms of different growth rates in different crystallographic directions [1, 2]. The work carried out during the 19th century laid a firm foundation for the modern scientific and technological developments in crystal growth.

Crystals are the pillars of modern technology. Crystals play a vital role in electronic industry, photovoltaic solar cells, fibre optic communications, detecting instruments, scintillators and in space technology. Integrated micro-electronics and opto-electronics necessitate improved crystal growth technology for large diameter silicon, GaAs and InP in combination with optimized defect and property control on submicron scale. Laser fusion technology depends on high power laser crystals and oxide crystals.

Crystal growth is a vital and fundamental part of materials science and engineering, since crystals of suitable size and perfection are required for fundamental data acquisition and for practical devices such as detectors, integrated circuits and for other millions and millions of applications. The ever increasing application of semiconductor based electronics creates an enormous demand for high quality semiconducting, ferroelectric, piezoelectric, oxide single crystals. Since there is a vast market for solid state devices, effort has been made in recent years on producing large size, good quality single crystals. Nowadays the growth of single crystals has assumed great impetus due to their importance both for academic research and technology.

Crystal growth is an inter disciplinary subject covering physics, chemistry, electrical engineering, metallurgy, materials science, crystallography, mineralogy, etc. In the recent years, direct visualization at atomic resolution of nucleic acid and variety of

proteins with which it interacts is possible by growing single crystals. Crystallography is concerned with the nature of the regular atomic arrangements within the crystal. Crystallographers had made remarkable studies about the crystal before the discovery of X-ray by crystals. However, only after that, it became possible to know about the internal arrangement of atoms in the crystals, in a more developed way. As there was a remarkable achievement in the study of internal atomic arrangements it lead to the study of more physical properties. This interest shifted from the study of natural crystals to the laboratory grown crystals.

The modern technology 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, piezoelectric, acousto-optic and photo-sensitive materials and crystalline films for microelectronics and computer industries. All these involve research in crystal growth and characterization.

The consistency of the characteristic of devices fabricated from a crystal depends on the homogeneity and defect content of the crystal. Hence, the process of producing single crystals which offers homogeneous media in the atomic level with directional properties, attracts more attention than any other process involved. 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.

1.3. Methods of Crystal Growth

Crystal growth is a controlled phase transformation to ordered solid phase, either from solid or liquid or gaseous phase. The growth units, namely the atoms or molecules, diffuse to the growth site from the mother phase, when given sufficient time to get orderly arranged on the lattice.

Single crystals can be considered as a regular polyhedral form bounded by smooth surfaces, which is assumed by a chemical compound, under the action of its interatomic forces, when passing from the state of liquid or gas to that of a solid under suitable conditions. Alternately, a single crystal can be considered as a homogeneous, anisotropic body having natural shape of a polyhedron and different directions. An ideal single crystal is the one in which every atom is surrounded by a precisely uniform spatial arrangements of other atoms and it is free from inner boundaries.

Growth of single crystals means careful arrangement of atoms, ions or molecules in the particular three dimensional order. It needs the careful control of a phase change. It is a non-equilibrium process and thought must be given to the temperature and concentration and other gradients and the fact that heat of crystallization is evolved and must be removed to the surroundings. At the same time, the crystal growth process must be as near-equilibrium and as near to a steady state process as possible. So, control of the crystal growth environment and consideration of growth kinetics both at the macroscopic and atomic levels are of vital importance to the success of a crystal growth experiment.

1.3.1. Classification

There are four major categories of crystal growth methods which are:

Solid state growth	→	Processes involving solid – solid phase transition
Vapour phase growth	→	Processes involving vapour – solid phase transition
Melt growth	→	Processes involving liquid – solid phase transition
Solution growth	→	Processes involving liquid – solid phase transition

Solution and melt growth methods are treated separately because growth from the melt is such a large and important category and also because solution growth methods differ much from methods used for pure melt growth. Various crystal growth techniques including the sub-categories [3] are shown in Figure 2. For additional knowledge on the growth of single crystals, it is suggested to refer the books by : Pamplin (Ed.) [3], Hartman [4], Brice [5], Mullin [6], Sangwal [7], Santhana Raghavan and Ramasamy [8], Byrappa and Ohachi [9], etc.

1.3.2. Solid state growth methods

Solid state growth technique can be considered as the conversion of a polycrystalline material into a single crystal by causing the grain boundaries to be swept through and pushed out of the material due to atomic diffusion. But, this is very slow at ordinary temperatures and is only rarely used.

1.3.3. Vapour growth methods

Single crystals with high purity can be grown from the vapour by sublimation and chemical vapour deposition. In this process, the source material to be crystallized is

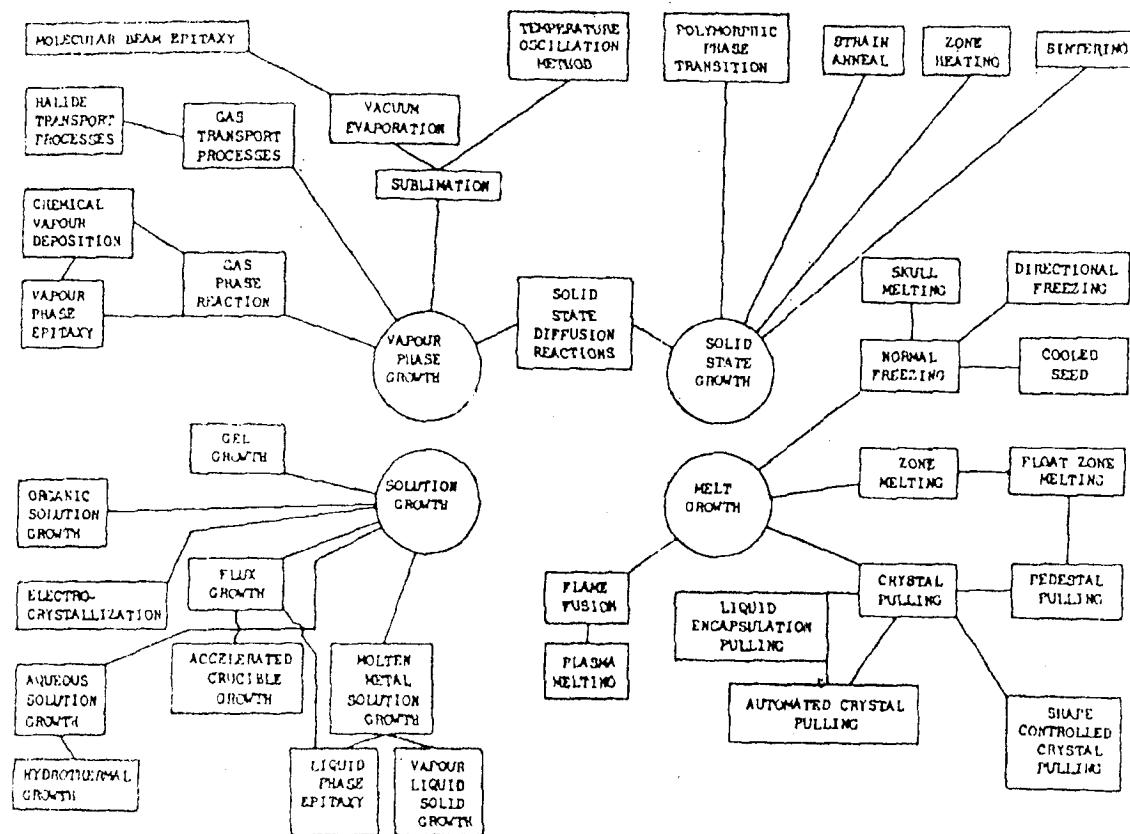


Figure 2: Categories of crystal growth techniques

provided from the vapour phase. Physical vapour deposition and chemical vapour deposition are the two widely used techniques. Deposition from the vapour phase is mostly used for the fabrication of thin layers of metal, insulator and semiconductor materials. The main advantage of this method is that it does not involve the contacting of the growing surface with a liquid or solid phase, thus avoiding numerous potential problems during and after the growth process.

1.3.4. Melt growth methods

The best method available for growing large single crystals of high perfection relatively rapidly is the melt method. This is employed for materials which melt congruently and has a manageable vapour pressure at the melting point. Most commonly used melt growth techniques are Bridgman and Czochralski (crystal pulling) methods.

1.3.5. Solution growth methods

Solution growth method is an ancient crystal growth method permitting crystal growth at a temperature well below the melting point. Materials which decompose on heating and/or which exhibit any structural transformation while cooling from the melting point can be grown by low temperature solution growth if suitable solvents are available. The supersaturation may be attained by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a colder region. In high temperature solution growth, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated.

When the crystal is in dynamic equilibrium with its parent phase, the free energy is at a minimum and no growth will occur. For crystal growth to occur this equilibrium must be disturbed by a change of a correct sign in temperature, pressure, chemical potential, electrochemical potential 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 the evolution of heat of crystallization. Normally, just one of these parameters is held minimally away from its equilibrium value to provide a driving force for the growth of crystal.

In the present study, we used only the low temperature aqueous solution growth method for the growth of single (sample) crystals. So, we do not present here the details of various methods used for the growth of single crystals. However, some details of low temperature solution growth methods are provided in Chapter 2.

1.4. Nonlinear Optics

Nonlinear optics is a topic of much current interest that exhibits a great diversity. This is due to the technological potentials of certain nonlinear optical effects for photonic based technologies. Applications of nonlinear optics include the frequency doubling of semiconductor lasers, the generation of ultra short laser pulses, optical information processing, telecommunications and integrated optics.

1.4.1. Origin of optical nonlinearity

The origin of nonlinear optical effects lies in the nonlinear response of a material to an electric field. In a dielectric medium, the charged particles are bound together.

When an electric field is applied, they are slightly displaced from their usual positions. This small movement of positive charges in one direction and the negative charges in the other, results in a collection of induced electric dipole moments. The effect of the field is to induce a polarization. The polarization of the molecule induced by an external field can be described by

$$P_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots,$$

where P_i is the component of the induced dipole moment in the coordinate direction i , α_{ij} is the polarizability tensor, β_{ijk} is the second-order polarizability or first-order hyperpolarizability tensor, γ_{ijkl} is the second-order hyperpolarizability tensor, E is the electric field strength at the locations of the molecule. The expression parallels that for the macroscopic polarization of a material,

$$P_i = \epsilon_0 [\chi^{(1)} E_j + \chi^{(2)} E_j E_k + \chi^{(3)} E_j E_k E_l + \dots].$$

In both equations the tensors are frequency dependent and should be written as functions of the frequency of the fields and the polarization produced. The linear term involving $\chi^{(1)}$ gives to the index of refraction, absorption, dispersion and birefringence of a medium. Most of the interesting nonlinear optical effects however arise from the terms of electric polarization which are quadratic or cubic in the electric field. The coefficients of the nonlinear terms are extremely small, but under proper circumstances they lead to striking effects. The quadratic polarization ($\chi^{(2)}$) gives rise to the phenomena of second harmonic generation, sum and difference frequency mixing, linear electro-optic modulation and parametric generation, etc, while the cubic term ($\chi^{(3)}$) is responsible for third harmonic generation, stimulated Raman scattering, optical bistability and phase conjugation.

Even order terms such as $\chi^{(2)}$ are nonzero only in non centrosymmetric media, whereas the $\chi^{(1)}$ and $\chi^{(3)}$ terms are nonzero in all media. Therefore centrosymmetric media do not exhibit second-order nonlinear effects, although third-order processes are possible in such media.

The high intensity available in the laser beam has made possible the observation of nonlinear effects at optical frequencies. Franken and co-workers [10] generally identified the birth of nonlinear optics with the experiment on second harmonic generation (SHG) of light by a ruby laser pulse in a quartz crystal. This discovery propelled the field of modern nonlinear optics and initiated intensive research in material science and crystal technology. In a short period following this discovery, several other nonlinear optical phenomena including parametric amplification and frequency mixing were identified, and many important concepts such as phase matching were quickly developed.

1.4.2. Nonlinear optical materials

The existence of harmonic light waves at the boundary of a nonlinear dielectric medium was predicted by Bloembergen and Pershan [11]. Nonlinear optical (NLO) phenomenon and the process occur within a nonlinear medium, usually a crystal [12]. This nonlinear optics is a vast area, and undoubtedly one of the most important areas of physics with a diverse range of applications.

An ideal NLO material should possess the following characteristics like large nonlinear figure of merit for frequency conversion, high laser damage threshold, fast optical response time, wide transparency window, architectural flexibility for molecular

design and morphology, ability to process into crystals, optical transparency (no absorption at fundamental wavelengths), ease of fabrication, non toxicity and growth environmental stability, high mechanical strength and thermal stability. Further, for exhibiting second order nonlinear effects, the material should crystallize in a noncentrosymmetric crystal class.

Since the first demonstration of harmonic generation, progress in nonlinear optics has always been dictated by the availability of better and newer materials. Traditionally the materials explored for NLO applications had been inorganic. Since nonlinearity and ferroelectricity have the same microscopic origin, efficient ferroelectrics were screened for NLO applications. This passive methodology was fairly successful in inorganics. But due to the inherent ionic nature of the bonds involved in inorganic materials, the nonlinearities available were often limited. Subsequent workers started exploring the molecular materials as candidates for SHG.

Organics, with their delocalized bonds and resonant enhancement of nonlinear susceptibility proved to be very handy. In addition to screening the known materials for NLO, organic chemists undertook to design newer materials with better nonlinearities [13-17]. This has resulted in a variety of materials with hitherto unknown extent of nonlinearities. However, most of these materials turned unsuitable for devices, due to their inherent limitations of mechanical strengths and linear optical properties. Circumstances forced material scientists to look for newer materials with a combination of favourable properties of both organics and inorganics and thus have paved way for research on semiorganics.

A new approach to high efficiency, optical quality organic based NLO materials is to consider compounds in which a polarizable organic molecule is stoichiometrically bonded to an inorganic host [18-20]. A typical example is zinc tris(thiourea) sulphate, ZTS, in which a distorted tetrahedron resulting from zinc in its coordination number IV is bonded to three thiourea molecules and a sulphate ion. An alternative to this approach is to form inorganic salts of chiral organic molecules. The phosphate salt of the chiral amino acid L-arginine, LAP, is an example of this class. The bonding schemes of these complexes are three dimensional, unlike the polar organic crystals, and hence result in stubbier habit faces. Contrary to intuition, that the inorganic would dilute the large hyperpolarizability available in organic systems, inorganic hosts often contribute enormously to the nonlinearity. This is because of the fact that many semiorganics have polymeric characters, effectively retaining the large polarizabilities of the organic systems.

Some of the important (inorganic, organic and semiorganic) NLO materials are listed (along with providing some of their physical properties) in Tables 1-3.

1.5. Present Investigation

Zinc tris(thiourea) sulphate (ZTS), $\text{Zn}(\text{NH}_2\text{CSNH}_2)_3\text{SO}_4$, is a relatively new and promising semiorganic nonlinear optical material for frequency conversion of high power laser. ZTS crystal shares the favourable polarizable property of the organic material and the mechanical properties of the inorganic material. Special features of this material are that it has a high laser damage threshold, a low UV cut off and is 1.2 times more

Table 1: Some important properties of inorganic NLO materials

Property	LiNbO ₃	KD*P	LiIO ₃	BBO	KTP	LBO	KNbO ₃
Point group	3m	42m	6m	3m	mm2	mm2	mm2
Transparency	350-5000	180-1800	340-4000	198-2600	350- 4500	160-2300	400-5500
Refractive Index (at 1064 nm)	n _o = 2.2322 n _e = 2.1560	n _o = 1.4931 n _e = 1.4582	n _o = 1.8567 n _e = 1.7168	n _o = 1.6551 n _e = 1.5425	n _x = 1.5737 n _y = 1.7395 n _z = 1.8305	n _x = 1.5649 n _y = 1.5907 n _z = 1.6052	n _x = 2.1194 n _y = 2.2195 n _z = 2.2576
D _{eff} (pm/V)	5.1	0.35	1.8	1.6	3.2	0.85	13
Threshold Power (MW)	0.70	30	66	13	0.029	Not available	Not available
Damage Threshold (GW/cm ²)	0.3 (10nsec)	5.0 (1nsec)	1.0 (0.1nsec)	23.0 (14nsec)	9-20 (1nsec)	1-14 (12nsec)	1.0 (10nsec)

Table 2: Some important properties of organic NLO materials

Property	MNA	POM	DAN	MMONS	MBANP	MAP
Point group	Mm2	222	2	mm2	2	2
Melting point (°C)	114	136	166	Not available	84	80.9
Transparency (nm)	480-2000	500-1700	485-270	510-2100	Not available	500-2500
Refractive Index	$n_x = 1.800$ $n_y = 1.600$ $n_z = ?$	$n_x = 1.663$ $n_y = 1.829$ $n_z = 1.625$	$n_x = 1.517$ $n_y = 1.636$ $n_z = 1.843$	$n_x = 1.530$ $n_y = 1.630$ $n_z = 1.961$	$n_x = 1.650$ $n_y = 1.714$ $n_z = 1.688$	$n_x = 1.507$ $n_y = 1.590$ $n_z = 1.843$
Nonlinear	$d_{11} = 60$	$d_{14} = 23$	$d_{22} = 12.4$	$d_{24} = 55$	$d_{22} = 8.3$	$d_{21} = 40$ $d_{22} = 44$ $d_{23} = 8.8$
Coefficient ($\times 10^{-9}$ esu)	$d_{12} = 90$	$d_{25} = 23$ $d_{36} = 23$	$d_{36} = 119$	$d_{32} = 41$ $d_{33} = 184$		
Damage threshold (GW/cm^2)	0.2	2.0	5.0	Not available	1.0	3.0

Table 3: Some important properties of semiorganic NLO materials

Property	dLAP	BTCC	ZTS	ATCC	ATMB	TSCCB
Point group	2	Mm2	Mm2	3m	3m	m
Melting point	130	185	<230	101	138	230
Transparency	250-1300	300-2000	300-2000	300-1500	330-1500	330-1420
Refractive indices at 1064 nm	$n_x = 1.4977$ $n_y = 1.5595$ $n_z = 1.5686$	$n_x = 1.6097$ $n_y = 1.7902$ $n_z = 1.8600$	$n_x = 1.6306$ $n_y = 1.6936$ $n_z = 1.6984$	$n_o = 1.6996$ $n_e = 1.6400$	$n_o = 1.7405$ $n_e = 1.6341$	$n_x = 1.7200$ $n_y = 1.7180$ $n_z = 1.8120$
Nonlinear susceptibility ($\times 10^{-9}$ esu)	$d_{14} = 0.22$ $d_{16} = 0.48$ $d_{22} = 0.68$	$d_{31} = 2.75$ $d_{32} = 0.2$ $d_{33} = 2.7$	$d_{31} = 0.31$ $d_{32} = 0.35$ $d_{33} = 0.23$	$d_{31} = 1.5$ $d_{32} = 0.7$ $d_{33} = 1.9$	$d_{31} = 0.27$ $d_{32} = 8.2$ $d_{33} = 2.7$	$d_{11} = 0.5$ $d_{11} = 0.3$ $d_{15} = 2.8$
d_{eff} (pm/V)	0.98	1.65	0.13	Not available	Not available	0.9
Damage threshold (GW/cm^2)	13.0	6.0	3.0	0.32	Not available	Not available

nonlinear than KDP (potassium dihydrogen orthophosphate). Also, ZTS crystal has excellent mechanical properties when compared to other semiorganic nonlinear optical crystals. Moreover, it is less hygroscopic than KDP [21]. ZTS belongs to the orthorhombic crystal system with the point group $mm2$ and the lattice parameters are $a = 11.130$, $b = 7.773$ and $c = 15.490\text{\AA}$ [22]. Several investigators have shown considerable interest on this material [21-43]. We suggest the readers to see Chapter 2 for a review of studies made on ZTS.

Newman et al [44] have found that the $\chi^{(3)}$ value of ZTS can be enhanced several times by doping (adding impurity). Anandakumari and Chandramani [45] have reported that KDP crystals containing alkali halide impurities have shown appreciable increase in second harmonic generation (SHG) efficiency compared to pure KDP crystals. Also, Sirdeshmukh et al [46] have found that impurity hardening in the case of rubidium halides. It can be expected that impurity addition to ZTS makes this material more useful.

Operation of electro-optic devices is based on the Pockel's effect, in which the change in the dielectric constant, $\Delta\epsilon_r$, is a linear function of the applied field [47]. Permittivity characterization may yield some useful information. Also, microelectronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant (ϵ_r) materials, as an interlayer dielectric (ILD) which surrounds and insulates interconnect wiring. Lowering the ϵ_r values of the ILD decreases the RC delay, lowers power consumptions, and reduces 'cross-talk' between nearby interconnects [48]. Recently, Goma et al [49] have found that 0.6 mol% urea addition to KDP leads to low permittivity value dielectrics.

The above features prompted a research programme to be carried out on the growth and physical properties of pure and impurity (various types) added ZTS single crystals.

We have grown ZTS single crystals by the free evaporation method and investigated the effect of three impurities (urea, Ni^{2+} and Mg^{2+}) added (impurity added with ZTS solution used for the growth of crystals) with five different impurity concentrations in each case on various properties of it.

Density was measured by using the flotation technique. X-ray diffraction (XRD) data were collected from the powder samples of the crystals using an automated X-ray diffractometer. The reflections were indexed and the lattice parameters were determined. In order to reveal the crystalline perfection of the specimen crystals grown, high resolution X-ray diffraction (HRXRD) curves were recorded.

Fourier transform infrared (FT-IR) spectral studies have been carried out on all the grown crystals. The important groups associated with the sample crystals were identified and their respective bands were assigned. Also, ultraviolet-visible (UV-Vis) spectral and photoluminescence (PL) studies were carried out.

Microhardness measurements have been carried out on the pure and impurity (1 mol% only) added crystals 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.

AC electrical measurements were carried out along the three (a-, b-, c-) directions by the parallel plate capacitor method at various temperatures ranging from 40-150°C for a fixed frequency of 1 kHz. The dielectric parameters, viz. ϵ_r , $\tan\delta$, σ_{ac} and E_{ac} were determined.

A report of the present investigation is provided in this thesis. The thesis is divided into five chapters with a list of literature cited (References) at the end of the thesis. We have already introduced the present work, in this first Chapter along with briefly giving the importance of single crystals, various methods of crystal growth, and an introduction to nonlinear optics phenomenon.

Chapter 2 gives a brief review of various studies made on ZTS single crystals in the near past. Growth of sample crystals and analyzing the quality by HRXRD studies are also dealt with along with providing some details of the low temperature solution growth methods. Chapter 3 deals with the density measurement, FT-IR spectral measurement, powder XRD studies, impurity concentration determination, and the hardness measurements. The results obtained in the SHG behaviour analysis, UV-Vis spectral and PL studies and dielectric measurements are reported and discussed in Chapter 4. Chapter 5 contains the summary and suggestions for future work in the same area of research.