CHAPTER-I

GENERAL INTRODUCTION AND RESEARCH OBJECTIVES

1.1 Introduction

Crystal growth plays a vital role in the modern technology and also in the areas of defence and space science. In addition, many crystals are useful in electro-optic devices, piezo-electric, accousto-optic, photo-refractive, photo-elastic, in radiation detectors, laser hosts, parametric amplifier, and transducers, harmonic generators, [1] etc.

Crystals are solids in which the atoms, molecules or ions are spaced in a regularly ordered repeated pattern extending in all three dimensions. The smallest group of atoms, molecules or ions is called the unit cell and a crystal is a combination of many unit cells. Crystals are grouped by their crystal structure into seven crystal systems. They are triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal and hexagonal. The periodic array of atoms repeated in groups, showing characteristic symmetry elements, throughout the entire material is called single crystal. Single crystals are the basis for the modern technology. The imperfections in crystals are useful in determining the physical and chemical properties of solids.

Modern technology is based on single crystals of semiconductors, dielectric, ferroelectric, superconductor, acousto-optic, nonlinear optical and optoelectronic materials [2]. The electronic industry makes use of crystals in filters, frequency controls, timer and circuits in cell phones, watches, clocks, television receivers, computers, navigational instruments and other products. Single crystals are also used for lasers, integrated circuits and data storage technology [3]. The development of optical communication systems has led to the need for nonlinear optical materials of high performance and used as components in optical devices [4]. Piezoelectric crystals find applications in electric lighter, stoves, piezoelectric transformers, piezoelectric sensors, detectors and generators of sound waves, industrial processing and several branches of engineering physics. Ferroelectric crystals are used in opto-electronics such as capacitors, non-volatile memory devices, high performance gate insulators, [5] etc. Photonic crystals find applications in various optical circuits such as wave guides, cavities, tapers, power spliters, filters [6] etc. Pyro elecric crystals are used for accelerating charged particles in vacuum or in gas [7]. Organic materials are in increasing demand as they possess large optical nonlinearity, and they are known by their applications in conductors [8], superconductor [9] as well as having nonlinear optical (NLO) and electro-optic device applications [10]. Semi organic NLO materials are widely used in the field of optical data storage, telecommunication, second harmonic generation (SHG) and optical signal processing [11], etc. Many amino acids have NLO properties [12]. L-Arginine phosphate is the first semi organic material discovered in 1983 [13]. A second order nonlinear material must have a large threshold and a large nonlinear optical coefficient [14]. The inorganic NLO materials have some advantages such as highest susceptibility and very good optical property. These materials have some disadvantages like absorption in the visible region, poor response time and degenerative photo refractive effects and poor optical transparency. Inorganic materials are high quality crystals show optical nonlinearity. The phenomenon of SHG in inorganic materials was first reported in 1961, which led to the extensive development of NLO materials such as inorganic semiconductor and photo-refractive crystals. Some of the examples are lithium niobate ($LiNbO_3$), potassium niobate ($KNbO_3$), Barium Titanate ($BaTiO_3$), Lithium Iodate ($LiIO_3$), the ferroelectrics are used as transducer materials in ultrasonics [8], potassium dihydrogen phosphate (KH_2PO_4), ammoniam dihydrogen phosphate ($NH_3H_2PO_4$) and semiconductors such as gallium arsenide (GaAs), cadmium sulphide (CdS), zinc germanium phosphide ($ZnGeP_2$), cadmium germanium arsenide ($CdGeAa_2$) are some of the infrared NLO materials [15-18].

Crystals of suitable size and perfection are used for devices such as detectors, integrated circuits. Due to large need of crystals, many methods for the growth of crystals have been used.

The thesis deals with the growth and various characterizations of some inorganic isomorphous NLO crystals and the results obtained from various studies are reported and discussed.

1.2 Types of crystals based on nature of bonding

Solids are classified into four types [19].

i) Molecular crystals in which the units occupying the lattice points are molecules.

ii) Covalent crystals in which the units are atoms.

iii) Metallic crystals in which the units are positive metallic ions surrounded by a ‘sea’ of electrons.

iv) Ionic crystals are composed of positively and negatively charged ions.

1.3 Isomorphism and mixed crystals

The notion of isomorphism was discovered by Mitscherlich who found that the crystal salts such as the hydrated potassium phosphate and arsenates are the hydrated potassium copper and iron sulphates were identical. The crystals are said to be isomorphous if (a) both have the same space group and unit cell dimensions and (b) the types and the position of atoms in both are the same expect for a replacement of one or more atoms in one structure with different types of atoms in other (isomorphous replacement), such as heavy atom, or the presence of one or more additional atoms in one of them (isomorphous addition). Isomorphous crystals can form solid solutions.

In crystallography, crystals are described as isomorphous if they are closely similar in shape [20]. Historically crystal shape was defined by measuring the angles between crystal faces with a goniometer. In modern usage isomorphous crystals belong to the same space group. Double sulphates such as Tutton's salt, with the general formula $M^1{}_2M^{11}(SO_4)_2 .6H_2O$ where M^1 is an alkali metal and M^{11} is a divalent ion of Mg, Mn, Fe, Co, Ni, Cu or Zn form a series of isomorphous compounds, though there are three series of alums with similar external structures, but slightly different internal structures. Many spinels are also isomorphous. In order to form isomorphous crystals two substances must have the same chemical formulation. They must contain atoms which have corresponding chemical properties and the sizes of corresponding atoms should be similar. These requirements ensure that the forces within and between molecules and ions are approximately similar and result in crystals that have the same internal structure. Even though the space group is the same, the unit cell dimensions will be slightly different because of the different sizes of the atoms involved. Sodium chlorate ($NaClO_3$) and sodium bromate ($NaBrO_3$) is an interesting couple of isomorphic inorganic compounds with quasy molecular anions. Other interesting isomorphic inorganic compounds are potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) and they are optically active crystals.

When two substances A and B have closely similar structures (isomorphous substances), with not very different cell dimensions, it is found that the atoms of one can replace those of the other indiscriminately in the lattice, resulting in a mixed crystal, say AB. The sizes of the atoms (or ions) and their electronic configurations are the other important considerations in this context. Any proportion of the two substances A and B may be contained in the crystal AB with cell dimensions intermediate between those of the components. Not all isomorphous substances form such mixed crystals, an example being calcite ($CaCO_3$) and sodium nitrate ($NaNO_3$) which have similar atomic arrangements, with approximately same cell dimensions. The corresponding ions are also close in size. But they do not form a mixed crystal, presumably because their solubility in water is extremely different. However one of them may grow on the other in parallel orientation and this is called 'oriented overgrowth' for which phenomenon, the conditions, such as isomorphism, are not necessary. Formal dimensional similarity on certain planes is adequate for such oriented overgrowth.

1.4 Nonlinear optics and the relevant materials

Nonlinear optics (NLO) is the study of optical properties of a material by the presence of intense light. Laser light is great intense to modify the optical properties of a material. The beginning of the field of nonlinear optics is the discovery of second harmonic generation by Franken et al in 1961, and after the demonstration of laser by Maiman in 1960. Second harmonic generation occurs due to the part of atomic response that depends quadratically on the strength of the applied optical field. The intensity of light generated at second harmonic frequency tends to increase square of the intensity of the applied laser light. Advantage of nonlinear optics is that it increases the number of wavelengths both shorter and longer than the original light.

When a light wave passes through a transparent dielectric material, the refractive indices of the medium are normally independent of the intensity of the light beam. If the light is of very high intensity, such as that available from a powerful laser, then in certain dielectric materials, the refractive indices are no longer constant. Refractive index (n) is a function of the electric strength vector E of the light wave which is given by

$$n(E) = n_o + n_1 E + n_2 E^2 + \ldots$$

where n_o is the refractive index in the absence of the electric field. Here n_1, n_2 and so on are the coefficients of the series expansion of n (E). This is the basis of the nonlinear optical effect. Crystals which exhibit non-linear optical effect are called non-linear optical crystals. The propagation of an intense light beam through a dielectric medium gives rise to alteration in the electrical charges as the electrons and atoms respond to the electro-magnetic fields in the wave. The main 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 small field strength, this polarization is proportional to the electric field E. In the nonlinear case, the re-radiation 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.

In a given material, the magnitude of the induced polarization P depends on the magnitude of the applied electric field E. The expansion of P in a series of powers of E is given by

$$P = \varepsilon_0 [\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots]$$

where $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$, etc define the medium response and are known as nonlinear susceptibility coefficients of first, second, third, etc [21] order respectively.

These are tensorial quantities that give a measure of the polarizing effect of the optical field on outer valence electrons. The magnitude of the susceptibilities is dependent on the chemical bonding of the materials. The first term in the expansion is responsible for the material's linear optical properties, and second and third terms give rise to diverse nonlinear three and four wave mixing processes, respectively. Second order susceptibility is non-zero only in non-centrosymmetric crystal structures. Three wave-mixing gives rise to phenomena like the second harmonic generation (SHG), optical rectification, linear electro-optic effect, sum and difference frequency generation and optical parametric oscillation. So, suitable nonlinear optical crystals are required to have laser sources at new optical wavelengths. For optical applications, a nonlinear optical material should have the properties such as wide optical transparency limit, large nonlinear figure of merit for frequency conversion, high laser damage threshold, wide phase matching angle, ability to process into crystals or thin films, ease of fabrication, non toxicity and good environmental stability and high mechanical strength and thermal stability**.**

NLO materials can be classified into three type viz. inorganic NLO materials, organic NLO materials and semiorganic NLO materials. Inorganic crystals are ionic bonded and easy to synthesis. They have high melting points. Some of the crystals were $NaClO_3$, $NaIO_3$, $NaBrO_3$, $LiNbO_3$ [16], $KNbO_3$, KDP, $BaTiO_3$ etc. Organic non- centrosymmetric meterials have much attention for application in photonic devices because of linear optical properties. NLO effects in organic molecules originate from strong donor-acceptor intermolecular interaction [22]. The dipolar aromatic molecules possessing an electron donor group and an electron acceptor group produce high second-order optical nonlinearity comes from intermolecular charge transfer between the two groups. Some of the acceptor and donor groups are given below.

Acceptor groups: NO_2, CN, COOH, COO^-, CF_3, N^{2+}, $C_2 (CN)_3$, CHO, CONHR, $CONR_2$, NH^{3+} and aromatic (R is alkyl group).

Donor groups: NH_2, $NHCH_3$, O^-, S^-, $COOCH_3$, OCH_3, SR, CH_3, OR, I, Br, Cl, F, NHR and aromatic. (R is an alkyl).

The magnitude of optical nonlinearities depends on the strength of donor – acceptor groups. The new class materials of hybrid inorganic-organic materials are known as the semiorganic materials. L-histidine tetrafluro borate [23], L-arginine phosphate [24], glycine lithium sulphate, L-alanine phosphate etc are the examples of semi organics.

1.5 Sodium chlorate ($NaClO_3$) and Sodium bromate ($NaBrO_3$)

It has been found that the crystalline properties of materials have applications in many devices such as laser resonators, polarizer, piezoelectric devices [25], crystal X-ray monochromators, scintillation detectors, holographic devices, iron selective electrodes substrate for thin films etc. Now a days the growth of nonlinear optical crystals are getting attention in the field of optical data storage, telecommunication second Harmonic generation and optical signal processing, etc. Good quality crystals are required for various applications which attracted many theoretical and experimental researchers.

Sodium chlorate and sodium bromate crystals are isomorphous [26] which have various applications like KDP crystal. Sodium chlorate is an inorganic compound with the chemical formula $NaClO_3$. It is a white crystalline powder that is readily soluble in water. It is hygroscopic. It decomposes above 250 °C to release oxygen and leave sodium chloride. Sodium chlorate is used as a non-selective herbicide. It is considered phytotoxic to all green plant parts [27].

Sodium bromate, the inorganic compound with the chemical formula of $NaBrO_3$, is the sodium salt of bromic acid. It is a strong oxidant, mainly used in continuous or batch dyeing processes involving sulfur or vat dyes and as a hair-permagent, chemical agent, or gold solvent in gold mines when used with sodium bromide.

Sodium chlorate and sodium bromate crystals belong to the cubic class of space group $P2_13$, lacking a centre of symmetry [28, 29]. By virtue of this symmetry, they display optical activity, both dextro and leavo forms crystallize from aqueous solutions [30]. These materials are halates exhibits miscibility in all proportions in the solid state. The crystal structures of $NaClO_3$, $NaBrO_3$ had been determined by Zachariasen [31] and Hamilton [32] and others. $NaClO_3$ and $NaBrO_3$ crystals have been investigated for their nuclear quadrupole resonance and summarized. The Cl^{35} resonance in $NaClO_3$ has been studied by Zeldes and Livingston [33] and the Br^{79} resonance in $NaBrO_3$ has been studied by Kushida et al [34].

1.6 Research objectives

The objectives of the present investigation are to

1. Determine the solubility of the materials.
2. Grow pure sodium chlorate, pure sodium bromate crystals and mixed sodium chlorate and sodium bromate crystals.
3. Grow sodium chloride, ammonium chloride, lithium chloride, and nickel sulphate doped sodium chlorate, doped sodium bromate crystals and doped mixed sodium chlorate, sodium bromate crystals.
4. Perform the EDAX analysis for pure sodium chlorate, pure sodium bromate and doped and mixed sodium chlorate, sodium bromate crystals
5. Carry out XRD studies
6. Determine the hardness using Vickers micro hardness.
7. Find out functional groups by FTIR spectral studies.
8. Study the transparency by UV-Visible -NIR spectral studies.
9. Carry out the SHG measurement by Kurtz- Perry powder technique.
10. Study thermal behaviour by TG/ DTA analysis.

11. Perform the capacitance and dielectric loss measurements, and to calculate the dielectric constant, AC conductivity and activation energy.
12. To study the surface features by scanning electron microscopy.

1.7 Chapterization

The first chapter contains the introduction part and objectives of the research work. The second chapter explains the experimental details of the different growth methods and the instrumentation adopted for the various characterization techniques. The crystallization and characterization of pure and doped sodium chlorate single crystals are covered in the third chapter. Growth and characterization of pure sodium bromate and doped sodium bromate single crystals are included in the fourth chapter. The fifth chapter presents the crystallization and characterization of mixed sodium chlorate and sodium bromate single crystals and lithium nitrate and nickel sulphate doped mixed sodium chlorate and sodium bromate single crystals. The summary and conclusions of the present work along with the scope for future work in the same area of research are given in the sixth chapter. Finally the resume of the candidate, list of publications and list of seminars/conferences attended/presented papers are given in the appendix section.