

CHAPTER I
EXORDIUM OF CRYSTAL GROWTH
AND NONLINEAR OPTICS

1. 1. Introduction

“You were in Eden, the garden of God; every precious stone adorned you: carnelian, chrysolite and emerald, topaz, onyx and jasper, lapis lazuli, turquoise and beryl.”

Ezekiel 28:13

Crystals are opus magnum of solids owing to their ordered pattern of atomic/molecular units. Their coloration and shining inspire people to tailor them in jeweler, magic, astrology, healing science also. Ancient civil society without any scientific knowledge handled stones for making fire, for haunting and for making shelter. Stones are peculiar mineralized structure. Swearing makes some white precipitate after dried. This was the first bio-inspired crystallization man could realized. Minerals dissolved in water could be precipitated after water dried. This helped men to know crystallization. Any material dissolved in any solvent could be restructured after the removal of that solvent. This curiosity about crystals, minerals and purification by crystallization still drives towards the intellectual study about materials. Quartz crystal is optically tuning the color of incident light beam after passing through it and paved the way for ‘Nonlinear optics’ (Franken 1961). Optical tunable crystals decorate the laser and photonics industries as energy harvesters. Crystals as ubiquitous, pollutant free energy resources call physicists, chemists, engineers, technologists to fabricate new crystals with desirable characteristics. This chapter briefs the historical remarks and philosophical thoughts of crystals. It also summarizes nonlinear optics and material selectivity and techniques.

1.2. Historical remarks of Crystals

Caves made of rocks and stones are the natural shelters for the animals and Homo sapiens. It was the first home embraced them to survive. This experience had genetically printed in human brain and life. The historiography of human civilizations are identified and named after materials they used. The ages are called as Stone Age, Bronze Age, Iron Age. Hardness and sharpness make stones as natural weapons for hunting and fire spark and some other domestic applications. Stones are hard objects endowed during the solidification of earth's crust entails various mineral molecules orderly patterned. Water and other volatile compounds were enriched in the magma are evaporated under hydrothermal conditions and large crystals and gemstones are formed in pegmatite and cavities. The very first bio-inspired crystallization process human observed was from swearing. Salt was precipitated after dried. Chinese Print of 2700 B.C and on Egyptian 'Papyrus Ebers' of 1500 B.C. incarnated that the people harvested salts from sea water evaporated. People could know the transformation of materials by recrystallization.

Zhoukoudian excavation report (Anderson 1934) remarked that Peking Man used stone tools made of quartz crystal for ceremonial and decoration also (Pei 1932). It was unearthed that quartz crystals were used by the prehistoric society in Singi Talav cave in India (D'Errico 1989). The excavation report by Layard at Nineveh uncovered the optical Nimrud lens made of crystals (Layard 1853). In order to engrave the names of sons of Israel, Priestly Garments were made by mounting twelve different precious stones namely carnelian, chrysolite and beryl; turquoise, lapis lazuli and emerald; jacinth, agate and amethyst; topaz, onyx and jasper (Exodus 28:17-20).

Silappathikaram, a Tamil epic sang about anklets, made of gold and filled with gemstones. Kannagi's anklet was filled with rubies and the anklet of Queen of Pandiya was filled with pearls. Titus Lucretius Carus (99-55 BC) in the book *De rerum natura* coupled the characteristics of solids with their atomic compositions (Brown 1997) He also ascended the solids diamond, quartz, iron and brass based on their hardness. Pliny the Elder (23-79 AD) in his book *Naturalis Historia* portrayed the habits of *quartz, iris, adamas and smaragdus*. He also described the rivers of Thessalia, fresh green groves are as clear as crystal over the gravelly stones. He narrated the purification of blue vitriol (Cupric sulphate) (Healy 1999). Vannoccio Biringuccio (1480-1539 AD) in *De Re Metallica* furbished the art of crystallization for purification of vitriol and alum (Smith 1942).

Homer coined the term 'crystallos' originates from the Greek 'cryos' (coldness) or 'crymos/crymyos' (frozen,ice) in the sense of frozen water. Ephiphanos, the Bishop of Cyprus already distinguished between 'crystallos hyd(r)atos' (crystal from water) and 'crystallos lidoi' (crystal of stone).

Early chemical knowledge from Indian subcontinent and China may have reached the Mediterranean region and contributed to the alchemical experiences in Alexandria and in the Roman Empire. Geber, an alchemist describes the purification of several salts by recrystallization. Alchemist tried to achieve a transmutation to gold, to a higher material, philosopher's stone. Conrad Gessner (1564) stated "*one crystal differs from another in its angle and consequently in its figure*" (Applebaum 2000). They mixed various agents and treated them with fire, this led them to crystallization phenomena. Philosopher's tinctura was prepared through extraction and recrystallization (Valentini 1769). Towards the end of the Middle Ages, the crafts for the synthesis of several salts by recrystallization were known and used on a pilot-

plant scale. Agricola investigated on the treatment of illness using magic power of specific crystals gemstones and minerals (Haeckel 1917). However the scientific breakthrough to chemistry, crystallography, physics and earth sciences and a certain scientific understanding of crystal growth had to wait three centuries.

In the 17th and 18th century, the fundamentals of crystallography and of the understanding of crystal formation was laid by the mathematicians Kepler and Descartes, the anatomists Steno and Bartholinus and the Physicians Hottinger and Cappeller. Cardano associated the hexagonal prismatic shape of quartz to the shape of cells in honeycomb while Kepler related the shape of snowflake to honeycomb. The hcp structure was linked with the arrangement of seeds in pomegranate by Kepler (Kepler 1611) and with cannonball in later by Raleigh (Kahr 2011). Huygens studied the cleavage of the Iceland Crystals and described double refraction and by the packing of flattened spheroids in 1660. Hooke observed the crystals formed after the urine frozen, through microscope and measured the angles in the flat type crystals using compass (Hooke 1665). Steno assumed the growth of crystals by superposition of new layers of minute particles and derived the law of constancy of crystal angles between crystal faces (Steno 1669). Baron von Linne systemized the minerals as rocks, ores and excavations and further classified the ores into salts, sulfurs and metals (Linnaei 1758). Carrangeot (1780) measured the angles between crystal faces by goniometer (Kraus 1918). Hauy hypothesized that crystals are aggregates of matter periodically arranged and he demonstrated the contact goniometer on Icelandic spar and observed the interfacial angles of emerald and beryl are constant and he also explained the law of symmetry (Hauy 1784). By later interfacial angles were measured by optical goniometer. The symmetry elements and the notation of crystalline faces introduced as reciprocals (Miller Indices) by Weiss. Ludwig (1826)

defined 32 crystal classes based on symmetry operations and periodical distribution of points. Bravais (1848) defined 14 lattices (Bravais 1866). Fyodorov defined 230 crystallographic space groups (Shafranovskiy 1963, Galiulin 2003). Ostwald determined the rate of crystallization in terms of activation energy rather than the lattice energy (Ostwald 1897).

The crystal habits are related to chemical species by Guglielmini (1688) and A.G. Werner (1774) later. The blow-pipe test gave the information in combination with physical properties like color, hardness, weight, smell etc. (Werner 1774). Haüy named the fundamental unit 'molecule', the group of atoms. He offered the molecular geometry which stresses that the shape of the molecules defines the shape of their primary aggregate and that substances differing in chemical composition can't occur in the same form (Haüy 1784). Dolomieu developed the molecular theory in chemical aspects. He postulated that superfluities allow the integrant molecules to assemble into same aggregate resulting pure homogenous system while pollutions deny assembling and making imperfections in the integrant molecular assembly. He also suggested that a chemical substance could exist in different solid forms and the same composition can have different molecules (Dolomieu 1801). Mitscherlich introduced 'isomorphism' (i.e. different composition, same morphology) after studying calcite and aragonite crystals and 'polymorphism (i.e.same composition, different morphology) (Mitscherlich1821)

After Malus (1809) who discovered the polarized light, Biot and Brewster, the theoretical aspects of symmetry could be proven by crystal optics. The discoveries of chemical elements, recognition of chemical reactions was of significance for recognizing the nature of crystals and crystal growth. The first realistic structure model of a simple binary compound by Barlow was of great value to the early

structure determinations after the discovery of x-ray diffraction (Barlow 1897). Steno contributed to crystal growth technique 'juxtaposition', through which crystals were grown by deposition of material on the external faces (Johnson 1932). Boyle had proven by several arguments that gemstones had crystallized from solutions (Boyle 1672). Rouelle studied the crystallization under the microscope (Rouelle 1745). Morveau supposed that all types of crystallization needed a preceding solution (Morveau 1778). Lowitz described about solution growth technique. He is known the first person who achieved the growth of beautiful and regular crystals by use of seed crystals (Lowitz 1795). The 19th century saw a large number of works on the recrystallization of salts from solution and of minerals from high temperature solutions with the help of solubility. The equilibrium habit of crystals was defined in the fundamental work on thermodynamics by J.W. Gibbs in 1878 and also by Curie in 1885 and by Wulff in 1901.

The 20th century has seen great discoveries like germanium transistor initiating (silicon) microelectronics, the first laser action observed between two as grown ruby crystal faces, GaAs faces leading to optoelectronics etc. The understanding of the crystal structure was initiated by the discovery of X-ray diffraction at crystal lattices by Von-Laue, in 1912. It evoked the structure determinations by W.L. Bragg from 1913 onwards and the development of X-ray techniques for single crystals and for powders, by which the crystal structures of inorganic and organic compounds, could be determined. Crystal growth technology was constantly developed along with the characterization methods to develop many compounds with specific desired properties like semiconductors, superconductors, nonlinear optical and electro-optical materials, ferroelectrics and solid state lasers. The 20th century has seen developments in the science of fundamental aspects of crystal growth and technology. Crystal growth is a

multidisciplinary subject and requires the collaboration of chemists, physicists, crystallographers; thermodynamicists, hydrodynamicists and engineers.

1. 3. Philosophical view on crystal

Philosophy was evolved from the efficient thinking of human minds. It deals with the reality, existence, knowledge, values, languages, logic and reasons. The ancient philosophy rose from, Indian subcontinent, China, Greek and Egypt (Chattopadhyaya D. 1968, Thilly F. 1965). Tamil Researcher Guna recounts the thought of Atomist Pakkudukkai Nankaniyar lived in Valluvar society (B.C. 6th Century) who advocated materials are designed by the fundamental elements namely Earth, Water, Air and Fire. He reaffirms Determinist Markali's hypothesis emphasized those forces of attraction and repulsion causing to explore bulk materials and to decompose into tiny particles (Guna 1996). Leucippus (5th century BC), atomist reckoned on everything made of indivisible atoms moving randomly in a vacuum (Long, AA 1999). The Greek Thinkers Leucippus and Democritus (400 B.C.) voiced that nature is made of two basic units namely atoms and void. Lucretius Carus (99-55 BC) acquainted 'hooked atoms' with density and hardness of the solids (Costa 1984). The Greek Philosopher Plato sounds in his words about the formation of the most perfect transparent crystals as *"The varieties of earth have been strained through water, changed into forms of heavy air and then squeezed so hard that it is no more soluble in water. The finer transparent stones consist of equal and homogeneous particles of earth"*. Aristotle promotes the change of one kind of material into another through his transmutation concept. It derived four fundamental properties of all materials as hot and moist in contrast to cold and dry. This led to research on the Philosopher's stone. (Kepler 1611, Steno 1669). Dolomieu in *Mineralogical*

Philosophy stated that all the chemical properties of a substance are the chemical properties of its molecules (Dolomieu 1801).

In his philosophical doctrine Weiner C. (1863) says “Regular arrangement of equal atoms takes place when every atom has placed the others around itself in a coincident manner”. Kitaigorodski conjectured about crystals made of closely packed constituent particles (Kitaigorodskii 1961). Modern Philosopher Kaunt accounts for self-organizing matter by natural forces and systematicity (Nuzzo A. 2005). In his thought, crystals are formed from matter fully dissolved in a fluid at rest, resulting from the evaporation. He pointed that the internal organizational tendency of matter plays a vital role of chemical affinity in the mixture of matters for the formation of masses and bodies. Simondon’s philosophy on crystallization briefs the physical individuation of crystal such that a seed crystal which individuates itself as an energetic system through a continuous amplification by triggering a process of individuation, when it is implanted in an amorphous substance in metastable state.(Piatti G. 2016). Deleuze (1989) influenced by Simondon connected the little crystalline seed and the vast crystallisable universe by quoting that everything is included in the capacity for expansion of the collection constituted by the seed and the universe.

1. 4. Crystal Growth Techniques

Crystal growth is a complex process involving bulk diffusion through the fluid, surface adsorption and diffusion, integration of ions and/or molecules into the crystal lattice and it depends on the reactivity of the crystal surface and saturation state of the fluid. (Nielsen 1984, Chernov 1984) It proceeds by successive transfer of atoms and arranging themselves to generate unit cells of crystal lattice one after another. Fig. 1. 1 depicts the classification of crystal growth techniques.

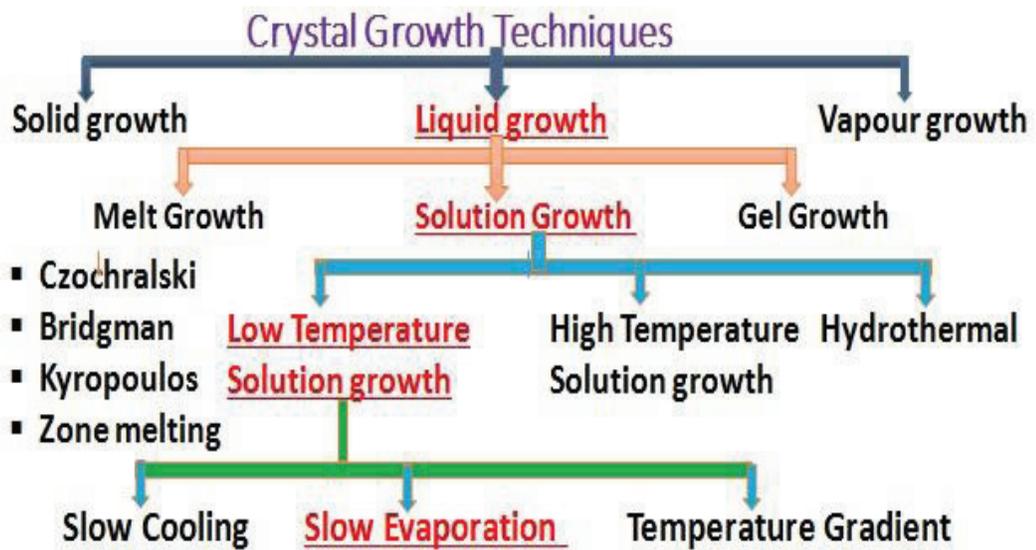


Fig. 1. 1. Crystal growth techniques

All crystal growth processes can be broadly classified based on the phase transformation and the physico-chemical process employing for crystallization. They are

- Growth from solid —————> Solid-solid phase transformation
- Growth from liquid —————> Liquid-solid phase transformation
- Growth from vapour —————> Vapour-solid phase transformation

1. 4. 1. Solid-Growth

The solid-state growth is a method where the resultant crystalline product is obtained from solid type starting material and the phase transformation is such that solid to solid. The conversion of a polycrystalline piece of material into single crystal by causing the grain boundaries to be swept through and pushed out of the crystal takes place in the solid-growth of crystals (Mullin 1972). NLO active crystal Barium selenostannate $Ba_6Sn_6Se_{13}$ was synthesized by mixing of BaSe, Sn and Se in the molar ratio of 6 : 6 : 7 under high temperature solid state reaction technique. It crystallized in $P2_12_12_1$ and due to mixed valence cations Sn^{2+} and Sn^{4+} (Feng 2013). It is basically controlled by atomic diffusion, used in metallurgical processes with techniques of annealing or sintering, quenching, etc. (Dhanraj 2010). $Cd_5(BO_3)F$ grown by high temperature solid state reaction method (Zou, 2013).

1. 4. 2. Growth from liquid

The liquid-state growth is a method where the crystalline product is harvested from liquid type starting material and the phase transformation is such that liquid to solid. The crystal growth from liquid can be broadly classified into categories namely

- a) Melt growth
- b) Solution growth and
- c) Gel growth

In these techniques, crystallization process is controlled by temperature, pressure and physicochemical mechanism in solutions.

1. 4. 2. (a) Melt Growth

Melt growth is the process of crystallization by fusion (melting) and resolidification of the pure material. It is the fastest of all crystal growth methods and is widely used for the preparation of large single crystals. Melt growth methods are limited to the materials which melt congruently and having an experimentally viable vapor pressure at its melting point. The material to be grown into crystal form is melted and after that it may progressively cooled to yield the crystalline matter. It is used worldwide for industrial crystallizations, including growth of metals, semiconductor crystals for electronic and computer chip making and laser industries. All materials of congruently melting compounds can be crystallized from the melt. Depending on the thermal characteristics, the following techniques are employed.

- i. Czochralski technique
- ii. Bridgman technique
- iii. Kyropoulos technique and
- iv. Zone melting technique

1. 4. 2. (a) i. Czochralski technique

Czochralski found that metals of low melting point could be crystallized via crystal pulling (Czochralski 1918). This technique consists of a crucible containing the charge material to be crystallized is surrounded by a heater capable of melting the charge. A pull rod mounted coaxially above the crucible is lowered to dip the seed crystal into the melt. The melt temperature is carefully adjusted until a meniscus is supported by the end of the seed. Once a thermal steady state has been achieved, the pull rod is slowly lifted and rotated and crystallization onto the end of the seed occurs.

Single crystals of useful size and perfection can be grown by this crystal pulling technique. $\text{Cd}_{1-x}\text{R}_x\text{Ca}_4\text{O}(\text{BO}_3)_3$ were grown by Czochralski method (Gheorghe, 2006). Optical quality crystal of $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ (Becker 2010) was grown by this method for nonlinear-laser applications. Crystals of tungstates (Zhao 2011), molybdates (Guo 2012, Lin 2013, Guo 2015) were grown by Czochralski method for electro-optical, magneto-optical, nonlinear optical and laser applications. $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (BTG) shows excellent second-order nonlinearity and electro-optical effects and was grown by Czochralski method (Liu 2015).

1. 4. 2. (a) ii. Bridgman technique

The pioneering work by Bridgeman was directed towards the growth of single crystals of mainly low melting point metals required for the high pressure studies. To obtain single crystals, he arranged for the initially self-seeded growth to be propagated through a capillary section in the growth ampoule in order to select a single grain. The relative translation of the crucible containing melt to the axial temperature gradient in a vertical furnace characterizes this technique. Bridgeman used a vertically mounted tubular electric furnace to melt the charge and lowered the ampoule containing the charge through it. Inorganic materials of tungsten, antimony, bismuth, tellurium, cadmium, zinc and tin were grown (Bridgeman 1925). This method was involving to grow SHG active crystals (Isaenko 2003) $\text{AgGa}_{1-x}\text{In}_x\text{Se}_2$ (Huang 2007), $\text{Ag}_{0.98}\text{Cu}_{0.02}\text{GaGe}_3\text{Se}_8$ (Fedorchuk 2011) and Pr^{3+} and Yb^{3+} doped Yttrium lithium fluoride single crystals (Hu 2012). An excellent multifunctional crystal Thallium arsenic selenide, Tl_3AsSe_3 (TAS) was grown (Singh 2016) in vertical Bridgman furnace where purification combined with low thermal gradient improves the quality of crystals. Singh (2016) identified that lower thermal gradient and low

growth rate are key to reduce thermal stresses in this ternary Tl-As-Se crystal was grown using a two zone vertical Bridgman furnace using capillary for nucleation.

High optical quality NLO crystals of $\text{BaGa}_2\text{GeS}_6$ and $\text{BaGa}_2\text{GeSe}_6$ were grown by Bridgeman-Stockbarger method. They crystallize in noncentro symmetric space group and suitable for mid IR applications (Badikov, 2016).

1. 4. 2. (a) iii. Kyropoulos technique

The Kyropoulos crystal growth technique (top seeded growth) was developed by Spyro Kyropoulos to grow single crystals of alkaline halides (Kyropoulos 1926). To initiate growth a cooled seed is dipped into the melt and the furnace temperature slowly cooled to encourage the downward growth of the crystal into the melt. Submerged growth like this allows the crystal to grow in a shallower thermal gradient than Czochralski process. Optically transparent NLO borate crystals (Kokh 2010), sapphire (Chen 2012) and other organic crystals (Pan 1994) were grown by this method. UV transparent single crystals of PbB_4O_7 and $\text{PbO}\cdot 2\text{B}_2\text{O}_3$ were grown by the top-seeded melt-growth method. It transmits UV light in the range of 240– 3600 nm with 80% (Bartwal 2001). Second order NLO crystals of SrB_4O_7 (SBO) (Pan 2010) have been grown by the Kyropoulos method. Second order NLO crystals CsB_3O_5 (Suzuki, 2010), RbTiOPO_4 (RTP) (Raj Kumar 2011) and $\text{NaBa}_4\text{Al}_2\text{B}_8\text{O}_{18}\text{Cl}_3$ (Zhang 2012, Fang 2013) were grown by Top Seeded Solution Growth (TSSG) method. Sapphire (Chen 2014) crystals were grown by this technique are suitable for LED (Bruni, 2015) technology. DUV NLO crystal $\text{GdAl}_3(\text{BO}_3)_4$ was grown in a new flux system $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--Li}_2\text{O--NaF}$ (Yue 2016). Optical transparent crystals $\text{Ba}_4\text{B}_{11}\text{O}_{20}\text{F}$ (Wu 2017) and polar crystals $\text{K}_3\text{B}_6\text{O}_{10}\text{Br}$ (Xia 2017) have been grown by top seeded solution growth technique. A potential mid-IR nonlinear optical

crystal Li_3VO_4 has been recently grown by top-seeded solution growth method (Chen 2017).

1. 4. 2. (a) iv. Zone melting technique

Zone melting technique was initiated in 1928 by Kapitza, who prepared single crystalline bismuth in a vertical glass tube (Kapitza 1928) and developed by William Gardner Pfann to prepare high purity materials mainly semiconductors for transistors (Pfann 1952). It is extended to any solute-solvent system having an appreciable concentration difference between solid and liquid phases at equilibrium. By passing a crystal bowl through a thin section of furnace very slowly, such that only a small region of the bowl is molten at any time, the impurities will be segregated at the end of the crystal. The bowl can grow as a perfect crystal if a seed crystal is placed at the base to initiate a chosen direction of crystal growth. It has the advantages of control of impurities while growth, reduce contamination of the melt by the crucible, less heater power, uniform doping obtained by zone refining, increase of grain size by zone refining. Semiconducting crystals of silicon (Gonik 2013) were grown by this technique. Single crystals of manganese orthosilicate (Mn_2SiO_4) (Tang 2012), Transparent and pale yellow calcium barium niobates ($\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$) single crystals (Ma 2014) and Cr, Nd:CaYAlO₄ (Ueda 2014), $\text{Co}_4\text{Nb}_2\text{O}_9$ (Cao 2015)

1. 4. 2. (b) Solution growth

The solution growth is also very popular for the growth of numerous crystals for industry. The growth of crystals by precipitation from aqueous solution is the most simple and the oldest technique. In this process, a saturated solution of the material to be grown into crystal is taken and in an appropriate solvent the crystallization takes place as this solution becomes critically supersaturated. The supersaturation can be achieved either by lowering the temperature of the solution or by slow evaporation.

The advantage of the method is that the crystals can be grown from a solution at temperatures well below its melting point, perhaps even at room temperature and, therefore, it turns out to be more applicable in many cases.

Solution growth can be broadly classified into

- i. High temperature solution growth,
- ii. Hydrothermal method and
- iii. Low temperature solution growth.

1. 4. 2. (b) i. High temperature solution growth

Crystal growth from high temperature solutions was widely used in the 19th century for minerals and for synthesis of new compounds. With the discovery of Vermeil's flame fusion growth, the difficulties encountered with nucleation control and growth of inclusion free crystals were solved. In the growth of crystals from high-temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturation may be promoted by evaporation of the solvent, by cooling the solution or by a transport process. The success of crystal growth from high temperature solution largely depends on the selection of the solvent system. This technique can be used for the crystallization of oxide compounds which generally have high melting points as well as for materials which have phase transitions below the melting point. Nonlinear Optical single crystals of KTiOPO_4 (Kannan 2005), Yttrium Calcium Oxy Borate (YCOB) (Arun Kumar 2008) and BPO_4 (Zhao 2012) were grown by this technique. A phase matchable Mid-IR NLO materials, Rb_2LiVO_4 and Cs_2LiVO_4 were synthesized by high-temperature solution method (Han 2017).

1. 4. 2. (b) ii. Hydrothermal growth

In this method, growth is usually carried out in steel autoclaves with gold or silver linings. The term hydrothermal means, literally, “hot water”. A number of metals, metal oxides and other compounds, practically insoluble in water up to its boiling point, show an appreciable solubility when the temperature and pressure are increased well below 100°C and 1 atmosphere, respectively. The requirements of high pressure cause practical difficulties and there are only a few crystals of good quality and large size grown by this technique (Ballman 1963). Quartz is the crystal grown industrially by this technique. Promising NLO single crystals of $\text{KBe}_2\text{BO}_3\text{F}_2$ and $\text{RbBe}_2\text{BO}_3\text{F}_2$ were grown by hydrothermal technique (McMillen, 2010). Crystals of $\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$, and $\text{Ba}_2\text{VSi}_2\text{O}_8$, all belonging to the fresnoite family were prepared (Abbott 2011). New rare potassium iodate $\text{K}(\text{IO}_3)$ was synthesized by using hydrothermal technique and compared its SHG efficiency with potassium borates. Phase matchable iodate produce second harmonics with more intensity than borates (Belokoneva 2012). Bulk size single crystals of $\text{Er}:\text{Sc}_2\text{O}_3$ Sc_2O_3 (McMillan 2012), Transition Metal mixed sulphate- sulphides (Yahia 2013) and $\text{Bi}_2\text{O}_2\text{CO}_3$ (Huang 2014) has been successfully developed by the hydrothermal method.

1. 4. 2. (b) iii. Low Temperature Solution Growth

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. It is particularly suited to those materials, which suffer from decomposition at high temperatures and which undergo phase transformations below the melting point. Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low temperature solution growth method. This method is the most widely used method for the growth of single crystals, when

the starting materials are unstable at high temperature (Pamplin 1979). This method is widely used to grow bulk crystals, which have high solubility and have variation in solubility with temperature (James 1975, Chernov 1984). Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low (Brice 1972). After undergoing so many modification and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Low temperature solution growth can be subdivided into the following methods:

- a) Slow cooling method
- b) Slow evaporation method and
- c) Temperature gradient method

1. 4. 2. (b) iii. a) Slow Cooling Method

Slow cooling is the easiest method to grow bulk single crystals from solution. However, the principal disadvantage of slow cooling method is the need to use a range of temperatures. The possible range of temperature is usually narrow and hence much of the solute remains in the solution at the end of the growth run. The use of wide range of temperatures may not be desirable because the properties of the grown crystals may vary with temperature. Temperature stability may be increased by keeping the solution in large water bath or by using a vacuum jacket. This technique needs only a vessel for the solution in which the crystals grow. The height, radius and volume of the vessel are so chosen as to achieve the required thermal stability. Achieving the desired rate of cooling is a major technological hurdle. This method also has the difficulty of requiring a programmable temperature controller. In spite of these disadvantages, the method is widely used with great success (Brice 1973). The

temperature at which crystallization begin is usually within the range 45-75°C and the lower limit of cooling is the room temperature.

Large high-optical-quality single crystals of diaqua(thiocyanato)manganese mercury-*N,N*-dimethylacetamide (Wang 2003) , potassium sulphate (Taboada 2003), L-histidinium bromide (Rajendran 2003), L-Arginine phosphate (Arunmozhi 2004) and thiosemicarbazide cadmium chloride monohydrate (Sankar 2007) were grown from aqueous solutions by the slow cooling method. Single crystals of Bis-Thiourea Zinc acetate have been grown by low temperature solution growth method using slow cooling process at an optimized pH of 3.5 (Jayalakshmi 2005). Organic SONLO Bis-Glycine Maleate (Balasubramanian 2010) and 2, 6-diaminopyridinium 4-nitrophenolate 4-nitrophenol (Chen 2012) and scintillating trans-stilbene (Carman 2013) were grown by temperature reduction in this method. Recently SHG active crystal sodium D-isoascorbate monohydrate (Rao 2013) and OH1 (2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene) malononitrile) (Li 2014) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ and cubic $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (Su 2015) also has been grown by slow cooling method. 4-hydroxy-3-methoxystyryl quinolinium (HMQ), single crystals with size up to $37 \times 6 \times 2 \text{ mm}^3$ are grown by slow cooling method. Intermolecular interactions with solvent molecules of methanol/toluene mixture were observed during the growth. Aromatic solvent mixtures exhibit a significantly different equilibrium between benzenoid and quinoid forms of the HMQ cation and slightly influence the crystal morphology (Lee 2016). Potassium Dihydrogen Phosphate (KDP) crystal doped with L-arginine (L-arg) amino acid with 1.4 wt% concentration in the solution was grown onto a point seed by the method of temperature reduction (Pritula 2016).

1. 4. 2. (b) iii. b) Slow Evaporation Method

In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. If the solvent is non-toxic like water, it is easy to allow evaporation into the atmosphere. The evaporation technique has the advantage to grow crystal at a fixed temperature. This technique needs a vessel for keeping the solution in which the crystals grow. The height, radius and volume of the vessel are properly chosen to achieve the required crystal size. A saturated solution heated slightly above its saturation temperature is poured into a screw-cap jar and a seed tied to a piece of thread is introduced to achieve the growth of the crystals. A second harmonic generative L-alaninium oxalate (Dhanuskodi 2004), L-histidine hydrochloride monohydrate (Madhavan 2007), L-Lysinium trifluoroacetate (Mathivanan 2008) were grown in aqueous solution by slow evaporation technique. Optically transparent glycine doped Bis Thiourea Cadmium Chloride (Dhumane 2009), 4-nitrophenol (Gandhimathi 2009) NLO single crystal were grown by slow solvent evaporation technique. Organic NLO crystals of Triketohydrindane hydrate (Kishore Kumar 2009) L-citrulline oxalate monohydrate (Sreevalsa 2011) 5-nitouracil (Okoth 2012) were harvested from aqueous solution. Single crystal of oxalic acid with good crystallinity was grown in aqueous solution and in acetone-water mixture. Cadmium based MOF Cd(LTP)₂ is crystallized in P2₁2₁2₁ space group slow evaporation of L-thioproline and water (Dong 2011) some NLO crystals namely 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (Sun 2012), 4-nitrophenol (Gandhimathi 2012) and 2,4,5-trimethoxy-4-bromochalcone (Patil 2014) were harvested. Glycine picrate was harvested in mixed solvent of acetone and double distilled water (Thilagavathy 2011). 2-Amino pyridine bithiourea zinc sulphate (Srineevasan 2013), L-asparagine-l-tartaric acid (LAsT) (Tamilselvan 2014) were

also grown by this method. Recently Second order NLO crystals of L-histidinium dipicrate dihydrate (Sethuram 2014) l-alanine strontium chloride trihydrate (Ignatius 2014), 4-methoxy-4'-chlorochalcone (Prabu 2014), 3-(4-chlorophenyl)-1-(pyridin-3-yl)prop-2-en-1-one (Menezes 2014), 4-methylpyridinium 4-hydroxybenzoate (Sudhakar 2014), bis (thiourea) silver (I) nitrate (Sivakumar 2014) were grown. L-methyl piperazinium 4-nitrophenolate-4-nitrophenol monohydrate (Nagapandiselvi 2015), Lithium sulfate monohydrate oxalate (Yadav 2015) L-histidinium dipicrate dehydrate (Helen 2015), anilinium perchlorate (Vivek 2015) and cis-2,6-bis(2-chlorophenyl)-3,3-dimethylpiperidin-4-one (Ponnuswamy 2015) have been grown.). α -lactose monohydrate (α -LM) single crystal has been grown in the solvent mixtures of DMSO and Water in various ratio by both slow and fast evaporation technique (Vinodhini 2015). Slow evaporation was recommended to grow α -LM with desired morphology. The reason was found to the adsorption of formamide and water in separate domains of fcc alkali halide crystals grown in aqueous solution by slow evaporation technique (Paestro 2016). Organic NLO single crystals of 5-chlorosalicylaldehyde (Babu 2015), Guanidinium Carbonate (Deepa 2016), piperazinium bis(4-hydroxybenzenesulphonate) (Pichan 2017) and organometallic crystal calcium bis-thiourea chloride (Anis 2016) were grown by this technique. Phase matchable metal molybdate crystal $\text{LiNa}_5\text{Mo}_9\text{O}_{30}$ was grown (Zhang 2016). Optical transmittance of cobalt chloride doped L-alanine crystals was lower than pure l-alanine grown by slow solvent evaporation technique (Ignatius 2016).

At room temperature, from aqueous solution, a new semi-organic NLO crystal tris thiourea magnesium zinc sulphate (Bhuvaneshwari 2015), Di Glycine Ammonium Sulfate (Helina 2016), Morpholinium dihydrogenphosphate (Rajan Babu 2016),

glycine admixture sodium molybdate NLO crystals (AmarsinghBhabu 2016). HCl added L-alanine monocrystal is grown by solution growth technique (Shkir 2016).

1. 4. 2. (c) Gel growth

For crystal growth of substances with very small solubility the diffusion method has been introduced in 1914 by Johnston (Johnston 1914) whereas crystallization from gels (Henisch 1970). The gel growth technique is a one kind of modified alternative version of solution growth technique in which the growth occurs due to reaction between two suitable reactants (solutions) in a gel medium or achieving super-saturation by diffusion in gel medium. It is the simplest technique under ambient conditions and well suited for the crystal growth of compounds, which are sparingly soluble and decompose at fairly low temperatures. Appreciable size of crystals of organic and inorganic components (Pandita 2001, Kusumoto 2005, Ramachandran 2014 and Ahmad 2015) were grown by gel medium.

1. 4. 3. Vapour-phase

The solid-state growth is a method where the crystalline product is obtained from vapour type starting material and the phase transformation is such that gas to solid. Vapor phase method is achieved by using specific chemical precursors in the form of vapor containing the desired elements. Vapor-phase growth primarily involves three stages: vaporization, transport, and deposition. The vapor is formed by heating a solid or liquid to high temperatures. Transportation of vapor may occur through vacuum, driven by the kinetic energy of vaporization. Deposition of the vapor may occur by condensation or chemical reaction. Vapor phase epitaxial technique is used to grow semiconducting materials. This method has the advantages of low dislocation density, low concentration of point defects. Vapor-phase growth is particularly employed in mass production of crystals for electronic devices because of

its proven low cost and high throughput, in addition to its capability to produce advanced epitaxial structures.

GaSe_{1-x}Te_x mixed crystals were successfully grown by liquid phase growth under controlled vapor pressure (Zhao 2017).

1. 5. Criteria for optimizing growth Parameters

The growth of good quality single crystals by slow evaporation and slow cooling techniques require the optimized conditions and the same may be achieved with the help of norms namely (i) Material purification, (ii) Solvent selection, (iii) Solubility, (iv) Solution preparation and crystal growth, (v) Seed preparation, (vi) Agitation (vii) Crystal habit, (viii) Cooling rate and (ix) Crystalline perfection.

Change in entropy is also adjudicating the growing interfaces in aqueous crystallization. The challenges involved in growing large single crystals from aqueous solution are solution preparation, crystallizer technology, bulk supersaturation control etc. Superheating a solution is advised to avoid spurious nucleation and emphasized high level of bulk supersaturation to attain a rapid growth (Bordui 1987). The variables which influence the crystal growth process of potassium chloride and copper sulfate in aqueous solutions were experimentally checked (McCabe 1929). They are listed as

- Nature of the solute
- Crystallographic structure of crystals
- Crystal habit of crystals
- Temperature
- Ratio of seed crystals to solution
- Rate of precipitation of material

- Weight ratio of product to seeds
- Agitator speed
- Screen analysis of seeds
- Initial unsaturation of solution.

1. 5. 1. Material Purification

An essential prerequisite for achieving success in crystal growth is the availability of high purity materials of both solute and solvents. Sometimes impurities may slow down crystallization process by being adsorbed on the growing face of the crystal, which changes the crystal habit (Buckley 1951). A careful repetitive use of standard purification methods of recrystallization followed by filtration of the solution would increase the level of purity.

1. 5. 2. Solvents Selection

An ideal solvent yields a prismatic growth habit and possesses characteristics such as high solute solubility, high and positive temperature co-efficient of solute solubility, low volatility, lower density than that of bulk solute and low viscosity. Solvents impact the morphology of the crystals (Davey 1986) by determining the orientation of the solute molecules on various faces in forming the different surface structures. Polar solvents influence on the growth and optical quality of the NLO active organic crystals (Thirupugalmani 2013).

1. 5. 3. Solubility

Solubility is an important parameter, which dictates the growth procedure. If the solubility is too high, it is difficult to grow bulk single crystals and too low solubility restricts the size and growth rate of the crystals. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal

growth to achieve the supersaturation in the solution. Low temperature solution growth is mainly a diffusion-controlled process in which the medium must be less viscous to enable faster transfer of the growth units from the bulk solution by diffusion. Supersaturation is an important parameter for the solution growth process. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process (Christian 1990). The concentration of the salt in solution depends on the chemical nature of the salt (Paestro 2016). The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined gravimetrically. A known quantity of the clear sample is analyzed. The solubility curve can then be plotted from the amount of solute dissolved and temperature by repeating the measurements for different temperatures.

1. 5. 4. Solution Preparation and crystal growth

For solution preparation, it is necessary to have an accurate solubility temperature data of the material. The saturated solution is prepared in accordance with the solubility curve. It is tested for saturation by suspending a small seed crystal in the solution. The temperature of the solution is slightly raised above the saturated temperature to dissolve any unwanted nuclei or any surface damage on the seed. The temperature is then lowered to the equilibrium temperature in order to initiate the crystal growth. Sintered glass filters of different pore size are used for solution purification. The clear solution saturated at the desired temperature is taken in a growth vessel. The seed crystal is suspended in the solution. The growth vessel is perfectly or partially closed during crystallization.

1. 5. 5. Seed Preparation

Defects present in an imperfect seed propagate into the bulk of the crystal, which decreases the quality of the crystal. Hence, seed crystals are prepared with care. The quality of the crystal is usually slightly better than that of the seed. Seed crystals are prepared by slow evaporation of the saturated solution. During this process, the surface of the seed inevitably gets damaged. This problem can be overcome by dissolving the deformed surface layers of the seed crystal, before commencing the growth. There would be a formation of many seeds from the solution as the concentration is high. But seeds of good visual quality free from inclusions and imperfections are selected for growth. Nucleation and growth mechanisms of salts from aqueous solution are as functions of supersaturation (Putins 2002). Nucleation of NaCl crystal in aqueous solution was examined (Chakraborty 2013).

1. 5. 6. Agitation

To have a regular and even growth, the level of super-saturation has to be maintained equally around the surface of the growing crystal. An uneven growth leads to localized stresses at the surface generating imperfection in the bulk crystals. Moreover, the concentration gradients that exist in the growth vessel at different faces of the crystal cause fluctuations in supersaturation, which seriously affect the growth rate of individual faces. The gradient at the bottom of the growth vessel exceeds the meta-stable zone width, resulting in spurious nucleation. The degree of formation of concentration gradients around the crystal depends on the efficiency of agitation of the solution. This is achieved by agitating the saturated solution in either direction at an optimized speed using a stirrer motor. The most prominent parameters for selecting a NLO crystal are listed in Table 1.1.

1. 5. 7. Crystal Habit

The growth of the crystal at approximately equivalent rates along all the directions is a prerequisite for its accurate characterization. This will result in a large bulk crystal from which samples of any desired orientation can be cut. Further, such large crystals should also be devoid of dislocation and other defects. These imperfections become isolated into defective regions surrounded by large volumes of high perfection, when the crystals grow with a bulk habit. The solvent effect on crystal habit was studied (Torgesen 1964). The factors affecting the growth rate in aqueous solution devised a mechanism to control the instantaneous cooling rate (Shie1994). The growth rates from aqueous solution as a function of impurity concentration and impurity effectiveness factor was related with surface coverage and step velocity (Kubota 1995). In the crystals which grow as needles or plates, the growth dislocation propagates along the principal growth directions of the crystals (Pamplin 1979). Changes of habit in such crystals, which naturally grow as needles or plates, can be achieved by any one of the following ways: Changing the temperature of growth, pH of solution and solvent and Adding a habit-modifying agent.

1. 5. 8. Cooling Rate

Supersaturation, the driving force which governs the growth of a crystal, is achieved by lowering the temperature of a solution. Temperature and supersaturation have to be precisely controlled for desirable results. The growth rate is maintained linear in order to grow large crystals. This requires an increase in the supersaturation level and linear cooling will not provide supersaturation. Hence, after the initial growth, the rate of temperature lowering is increased. Operation within the metastable limit occurs without any spurious nucleation in the solution. A large cooling rate changes the solubility beyond the metastable limit.

Table 1.1. Parameters for selecting a NLO crystal

LASER PARAMETERS	CRYSTAL PARAMETERS
NLO process	Type of phase-matching, d_{eff}
Power, Repetition rate	Damage threshold
Divergence	Acceptance angle
Bandwidth	Spectral acceptance
Beam size	Crystal size, Walk off angle
Pulse width	Group velocity mismatching
Environment	Moisture, temperature acceptance

Further, fluctuations in supersaturation may encourage solution inclusions of flaw in growing crystals (Wilcox 1983). Hence, a balance between the temperature lowering rate and the growth rate has to be maintained.

1. 5. 9. Crystal Perfection

The perfection of the grown crystal is based on purity of the starting materials, quality of the seed crystal, cooling rate employed and efficiency of agitation. Hence, high quality single crystals can be grown from quality seeds.

1. 6. Concepts of Nonlinear Optics

The process of light-matter interactions emerges various phenomena in the day-to-day life. One of the fascinating events based on light-matter interaction is optical phenomena. When the light such as electromagnetic waves propagates along the crystalline medium, the molecules get electrical polarization. The optical properties of a medium depend upon the intensity of the light. Due to these polarizing facts the transmitting light get changes in its properties like frequency, color shape and size. This kind of optical phenomena is classified into linear and nonlinear optics which depends upon the relation between the applied electric field (**E**) and polarizability (**P**) of the medium. Linear optics is the optics of weak light where the intensity of the light is low and light is deflected or delayed but its frequency is unchanged because of the polarizability (**P**) is in linear response to applied electric field (**E**). Nonlinear optics is Optics of intense light where light's frequency is altered due to the nonlinear relation between the applied electric field (**E**) and polarizability (**P**) of the medium.

1. 6. 1. History of development in Nonlinear Optics

The development of the theoretical understanding of NLO crystals can be divided basically into three periods. The first period was from 1961 to mid-1960s.

Optical second harmonic generation (SHG) was discovered in quartz crystal in 1961 (Franken 1961). They observed ultraviolet light at twice the frequency of a ruby laser ($\lambda = 6493 \text{ \AA}$), when the light was made to traverse a quartz crystal as shown in Fig. 1.

2. This experiment attracted widespread attention and marked the beginning of the experimental and theoretical investigation of nonlinear optical properties. In this stage, the NLO response of matter was recognized only in theory to depend upon the susceptibilities $\chi^{(n)}$ and the applied optical electric fields as

$$\mathbf{P} = \chi\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \dots,$$

The ratio of successive terms in the polarization \mathbf{P} can be described approximately by

$$P^{(n+1)}/P^n \approx E/E_{at}$$

Here E is the applied electric field and E_{at} is the atomic field strength with the absolute value $E_{at} \sim 3 \times 10^8 \text{ V/cm}$ (Bloembergen 1965) in general. It is well known that two facts have been implied regarding NLO effect. The first one is that NLO effects on matter can be observed only with a sufficiently powerful source.(i.e.) applied electric field should acquired the value comparable to the atomic field strength. The second one is that NLO effects, cannot be generated if the structure of a crystal or other matter is centric. It was this important conclusion that enabled scientists to search for NLO materials successfully among the numerous known piezoelectric, ferroelectric, and electro-optical crystals. KDP-type NLO materials were thus found on the basis of this idea.

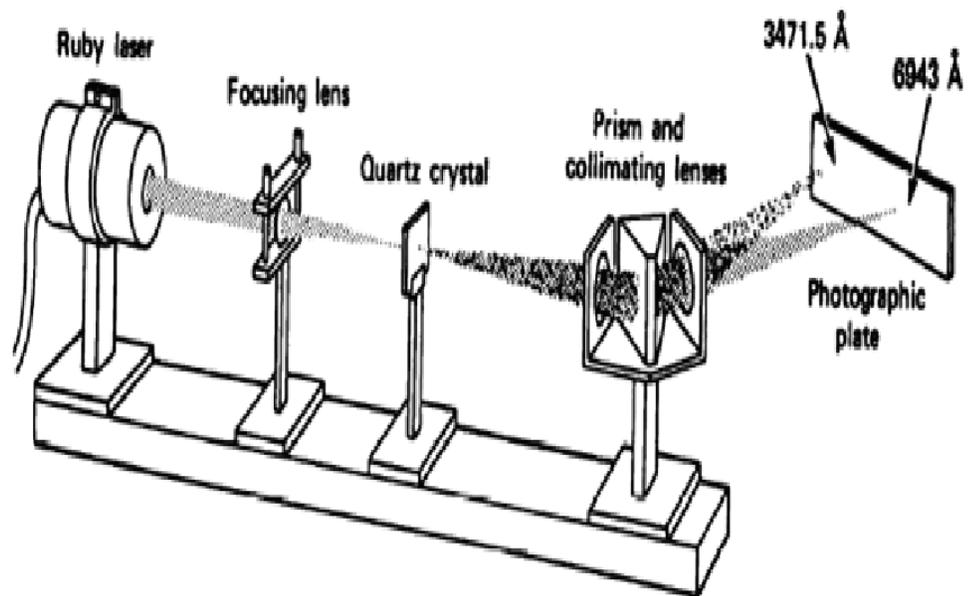


Fig. 1. 2. Experimental Demonstration of Second Harmonic Generation

The second stage in the theoretical understanding of NLO crystals was from the mid-1960s to the beginning of the 1980s. Scientists began to study the relationship between the macroscopic properties of NLO crystals and their microscopic structures. The charge transfer model of conjugated organic molecules with donor– acceptor radicals and the anionic group theory of NLO effect on crystals are the two major representatives of this kind of work. Kurtz and Perry (1968) at the Bell Laboratories in 1968 developed a powder NLO test technique that permits rapid evaluation of the order of $\chi^{(2)}$ coefficients and the determination phase matching in powder samples without the growth of single crystals. Then, in 1978, Halbout and Tang improved this technique by using a dye laser source to decide SHG coefficient with phase-matchable region (Hallbout 1981).

The third stage of the development started in the mid-1990s started with rapid increase in computational capability (Payne 1992) and continues to the present. Computer program with the Gaussian '92 package and can easily calculate the SHG coefficients for almost all major NLO crystals. The first-principles energy band calculation method was introduced to evaluate other important optical parameters of NLO crystals, that is, band gap and refractive indexes, birefractive indexes in particular. A plane wave pseudo-potential total energy package, CASTEP 3.5 program developed a new method to calculate the SHG coefficients, band gap, and refractive indexes, and at the same time, to analyze the contribution of cation and anionic groups separately to the SHG coefficient in NLO crystals.

1. 6. 2. Mathematical description for nonlinear optics

A linear dielectric medium is characterized by a linear relation between the polarization density and the electric field,

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad \text{----- (1)}$$

where ϵ_0 is the permittivity of free space and χ is the electric susceptibility of the medium.

The nonlinearity may be of microscopic or macroscopic origin. The polarization density $\mathbf{P} = Np$ is a product of the individual dipole moment p induced by the applied electric field \mathbf{E} and the number density of dipole moments N . The nonlinear behaviour may reside either in p or in N . The relation between p and E is linear when E is small, but becomes nonlinear when \mathbf{E} acquires values comparable to interatomic electric fields, which are typically $10^5 - 10^8$ V/m. This may be understood in terms of a simple Lorentz model in which the dipole moment is $p = -ex$, where x is the displacement of a mass with charge $(-e)$ to which an electric force $(-eE)$ is applied. If the restraining elastic force is proportional to the displacement (i.e., if Hooke's law is satisfied), the equilibrium displacement x is proportional to \mathbf{E} . In that case \mathbf{P} is proportional to \mathbf{E} and the medium is linear. However, if the restraining force is a nonlinear function of the displacement, the equilibrium displacement x and the polarization density \mathbf{P} are nonlinear functions of \mathbf{E} and, consequently, the medium is nonlinear.

The relation between \mathbf{P} and \mathbf{E} is then approximately linear for small \mathbf{E} , deviating only slightly from linearity as \mathbf{E} increases. The nonlinear optical response of a material system to an applied optical wave can be described by expressing the material polarization $\mathbf{P}(t)$ as a power series expansion in the applied electric field $\mathbf{E}(t)$ as

$$\mathbf{P} = a_1 \mathbf{E} + \frac{1}{2} a_2 \mathbf{E}^2 + \frac{1}{6} a_3 \mathbf{E}^3 + \dots, \quad \text{----- (2)}$$

and it suffices to use only a few terms. The coefficients a_1 , a_2 , and a_3 are the first, second, and third derivatives of \mathbf{P} with respect to \mathbf{E} , evaluated at $\mathbf{E} = 0$. These coefficients are characteristic constants of the medium. The first term, which is linear, dominates at small \mathbf{E} . Clearly, $a_1 = \epsilon_0 \chi$ where χ is the first order linear susceptibility, which is related to the dielectric constant and the refractive index of the material by

$$n^2 = \frac{\epsilon}{\epsilon_0} = 1 + \chi \quad \text{----- (3)}$$

The second term represents a quadratic or second-order nonlinearity, the third term represents third-order nonlinearity, and so on. It is customary to write an equation

$$\mathbf{P}(\mathbf{t}) = \epsilon_0(\chi\mathbf{E}(\mathbf{t}) + \chi^{(2)}\mathbf{E}^2(\mathbf{t}) + \chi^{(3)}\mathbf{E}^3(\mathbf{t}) + \dots), \quad \text{----- (4)}$$

Eqn. can be rewritten as

$$\mathbf{P} = \epsilon_0\chi\mathbf{E} + 2d\mathbf{E}^2 + 4\chi^{(3)}\mathbf{E}^3 + \dots, \quad \text{----- (5)}$$

Equating the coefficients in Eqn. (2) and (5), we can get

$d = \frac{1}{4}a_2$ and $\chi^{(3)} = \frac{1}{24}a_3$ describing the strength of the second and third-order nonlinear effects, respectively. Equation (5) provides the essential mathematical characterization of a nonlinear optical medium; where $\chi^{(2)}$ is the second order nonlinear susceptibility and $\chi^{(3)}$ is the third order nonlinear susceptibility.

Suppose now that the field incident on a medium has the form of

$$\mathbf{E} = \mathbf{E}_0 \cos(\omega t) \quad \text{----- (6)}$$

Substituting this in eqn (4), we have

$$\mathbf{P}(\mathbf{t}) = \epsilon_0(\chi\mathbf{E}_0 \cos(\omega t) + \chi^{(2)}\mathbf{E}_0^2 \cos^2(\omega t) + \chi^{(3)}\mathbf{E}_0^3 \cos^3(\omega t) + \dots) \quad \text{-- (7)}$$

Using the trigonometric relations

$$\cos^2\theta = \frac{1+\cos 2\theta}{2} \text{ and } \cos^3\theta = \frac{\cos 3\theta + 3\cos\theta}{4}$$

We can transform the eqn.(7) to the form

$$\begin{aligned}
\mathbf{P}(t) = & \\
& \varepsilon_o \left(\chi \mathbf{E}_o \cos(\omega t) + \frac{1}{2} \chi^{(2)} \mathbf{E}_o^2 + \frac{1}{2} \chi^{(2)} \mathbf{E}_o^2 \cos(2\omega t) + \frac{1}{4} \chi^{(3)} \mathbf{E}_o^3 \cos(3\omega t) + \right. \\
& \left. \frac{3}{4} \chi^{(3)} \mathbf{E}_o^3 \cos(\omega t) + \dots \dots \right) \quad \text{----- (8)}
\end{aligned}$$

We can obtain

$$\begin{aligned}
\mathbf{P}(t) = & \frac{1}{2} \varepsilon_o \chi^{(2)} \mathbf{E}_o^2 + \varepsilon_o \left[\chi + \frac{3}{4} \chi^{(3)} \mathbf{E}_o^2 \right] \mathbf{E}_o \cos(\omega t) \\
& + \frac{1}{2} \varepsilon_o \chi^{(2)} \mathbf{E}_o^2 \cos(2\omega t) + \frac{1}{4} \varepsilon_o \chi^{(3)} \mathbf{E}_o^3 \cos(3\omega t) \quad \text{----- (9)}
\end{aligned}$$

The first term is a constant term accounts to d.c. field across the medium, the effect of which is of comparatively little practical importance. The second term follows the external polarization and is called first order harmonic of polarization. The third one oscillates at frequency 2ω and is called the second harmonic of polarization and the fourth term is called third harmonic of polarization.

In centrosymmetric media, which have inversion symmetry so that the properties of the medium are not altered by the transformation $\mathbf{r} \rightarrow -\mathbf{r}$, the $\mathbf{P}-\mathbf{E}$ function must have odd symmetry, so that the reversal of \mathbf{E} results in the reversal of \mathbf{P} without any other change. The second-order nonlinear coefficient d must then vanish, and the lowest order nonlinearity is of third order.

1. 6. 3. Phenomenon associated with Nonlinear optics

A number of interesting optical phenomena arise from the second and third order susceptibilities. For example, $\chi^{(2)}$ gives rise to second harmonic generation (Kurtz 1968), d.c. rectification (Bass 1962), the linear electro-optic effect or Pockels effect (Franken 1963), parametric oscillation (Giordmaine 1965), and three-frequency processes such as mixing (Wang 1965) and sum generation. The third order susceptibility is responsible for third harmonic generation (Terhune 1962), the quadratic electro-optic effect or Kerr effect (Minck 1966), two-photon absorption

(Kaiser 1961), and Raman (Eckhart 1962), Brillouin (Chiao 1964), and Rayleigh (Mash 1965) scatterings. Typical values of the second-order nonlinear coefficient d for dielectric crystals, semiconductors, and organic materials used in photonics applications lie in the range $d = 10^{-24}$ – 10^{-21} (C/V² in MKS units). Typical values of the third-order nonlinear coefficient $\chi^{(3)}$ for glasses, crystals, semiconductors, semiconductor-doped glasses, and organic materials of interest in photonics are in the vicinity of $\chi^{(3)} = 10^{-34}$ – 10^{-29} (Cm/V³ in MKS units). An applied optical electric field incident on a nonlinear optical medium in the form of

$$\mathbf{E} = \mathbf{E}_1 \cos(\omega_1 t) + \mathbf{E}_2 \cos(\omega_2 t) \quad \text{----- (10)}$$

The polarization can be obtained in the form of

$$\mathbf{P}(\mathbf{t}) = \epsilon_o(\chi\mathbf{E}(\mathbf{t}) + \chi^{(2)}\mathbf{E}^2(\mathbf{t}) + \chi^{(3)}\mathbf{E}^3(\mathbf{t}) + \dots),$$

So, the second order nonlinear term can be calculated as

$$\begin{aligned} \mathbf{P}_{NL}(\mathbf{t}) &= \epsilon_o\chi^{(2)}\mathbf{E}^2(\mathbf{t}) = \epsilon_o\chi^{(2)}[\mathbf{E}_1 \cos(\omega_1 t) + \mathbf{E}_2 \cos(\omega_2 t)]^2 \\ \epsilon_o\chi^{(2)}\mathbf{E}^2(\mathbf{t}) &= \epsilon_o\chi^{(2)}[\mathbf{E}_1^2 \cos^2(\omega_1 t) + \mathbf{E}_2^2 \cos^2(\omega_2 t) \\ &\quad + 2\mathbf{E}_1\mathbf{E}_2 \cos(\omega_1 t) \cos(\omega_2 t)] \end{aligned}$$

By using the trigonometric relations

$$\cos^2\theta = \frac{1+\cos 2\theta}{2} \quad \text{and} \quad 2\cos A \cos B = \cos(A+B) + \cos(A-B)$$

By redefining the equation as

$$\begin{aligned} \epsilon_o\chi^{(2)}\mathbf{E}^2(\mathbf{t}) &= \frac{1}{2}\epsilon_o\chi^{(2)}[\mathbf{E}_1^2 + \mathbf{E}_2^2] \rightarrow \text{d.c. rectification} \\ &+ \frac{1}{2}\epsilon_o\chi^{(2)}[\mathbf{E}_1^2 \cos(2\omega_1 t)] \rightarrow \text{Second Harmonic Generation} \\ &+ \frac{1}{2}\epsilon_o\chi^{(2)}[\mathbf{E}_2^2 \cos(2\omega_2 t)] \rightarrow \text{Second Harmonic Generation} \\ &+ \epsilon_o\chi^{(2)}\mathbf{E}_1\mathbf{E}_2 \cos(\omega_1 + \omega_2) \rightarrow \text{Sum Frequency Generation} \\ &+ \epsilon_o\chi^{(2)}\mathbf{E}_1\mathbf{E}_2 \cos(\omega_1 - \omega_2) \rightarrow \text{Difference Frequency Generation} \end{aligned}$$

The nonlinear effects arises from second order nonlinear susceptibility $\chi^{(2)}$ and their corresponding mathematical terms are correlated.

1. 6. 3. (a) Second harmonic generation (SHG)

Second Harmonic Generation (SHG) is a special case of frequency mixing occurs when both input frequencies are equal. The frequency of the output is thentwice the frequency of the input and the interaction is known as Second Harmonic Generation (SHG). It is denoted in Fig.1. 3.

1. 6. 4. Applications of NLO crystals

NLO Laser crystal is used as optical spanner (Allen 1992, Simpson 1997). When a pulsed laser is propagating through some crystals, they generate a coherent supercontinuum (Udemn 2002, Cundiff (2003). Diffraction-free propagation was achieved in photonic NLO crystals with minimum input power (Christodoulides 2003). High efficient SHG at blue light region was measured in KNbO₃ crystal doubling the frequency of pico second pulsed laser (Li 2003). Blue laser was generated by Cd_{1-x}R_xCa₄O(BO₃)₃ (R=Sc, La) inorganic crystal which converted the frequency of laser from Ti:Sapphire laser source (Gheorghe, 2006). Silicon laser was generated through Raman amplification in Silicon crystalline layers (Rong 2005). Green light was harvested from a silicon photonic-crystal waveguide by slow-light-enhanced third harmonic generation.(Corcoran 2009). A spontaneous parametric down-conversion SPDC nonlinear optical crystal was placed inside a passive optical cavity, and UV femtosecond laser pulses with multiphotons entangled states were produced for quantum information (Krischek 2010). Stochastic resonances were occurred through NLO crystals, to scramble and de-scramble the optical image (Wiersma 2010).

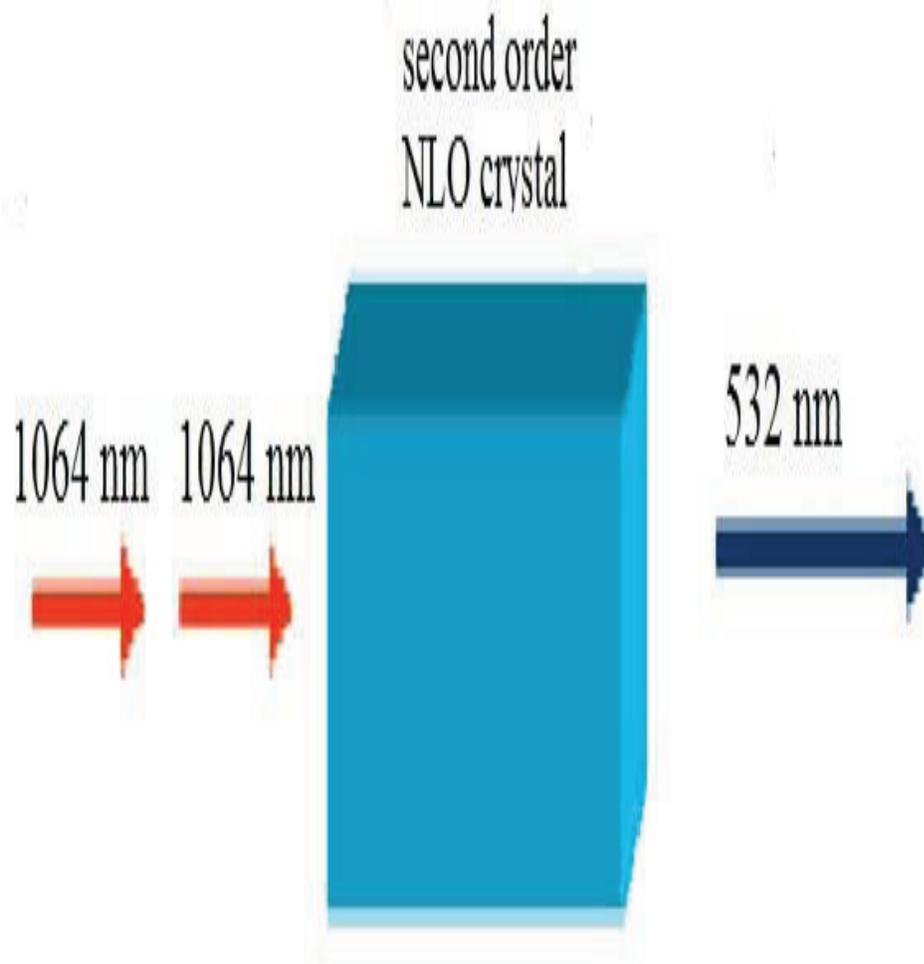


Fig. 1. 3. Second Harmonic Generation in a NLO Crystal

CsB₃O₅ NLO single crystal transmitted UV lights about 85% and yielded green laser by doubled the frequency of Nd:YAG laser with 60% (Suzuki 2010). Deep UV NLO crystals are useful in lithography (Jain 1982, Pol 1986), Fluorescence detection (Schulze 2005), Photochemistry (Dulcey 1991), Surface-enhanced Raman scattering (Daniel 2013). Optical solitons were generated in crystalline micro resonators by balancing nonlinearity and dispersion (Herr 2014). Structural analysis (Schlichting 2015) and time-resolved molecular imaging (Tenboer 2014) techniques have been improved by X-ray free-electron lasers (XFELs) in macromolecular crystallography.

Optical SHG is very useful to study nonlinear coefficients and geometry-dependent optical in-coupling coefficients of single-crystalline II–VI semiconducting nanowires, nanobelts, and nanoflakes on which transmission electron microscopy measurements cannot be typically performed (Ren 2015). Crystallographic orientations in single ZnS nanowires have been precisely determined using SHG microscopy (Hu 2015). The small fraction of an anisotropically distributed twin-crystal lattice weakly breaks the inversion symmetry in a microstructure KDP single crystal belongs to Monoclinic P2₁/c which is a centrosymmetric space group, resulting in small second-order susceptibility (Ren 2016). Doppler Shift has been performed during SHG in a NLO crystal with three-fold rotational symmetry whose optical axis is aligned along the propagation direction of light (Li 2016). The nonlinear optical Kerr effect has been utilized in Tb₃Ga₅O₁₂ crystal at a cryogenic temperature of 1.7 K to modulate the polarization of light at terahertz frequencies (Subkhangulov 2016). Green light laser was second harmonically generated from Tricyclic calcium nitrate NLO single crystal (Peter 2016). Pulsed laser is used for annealing to introduce dopants in crystals GeSn, Ge, SiC suitable for MOSFET. After the laser irradiation, the Ge_{1-x}Sn_x:Sb molecules were recrystallized in 100 ns time (Horiuchi 2017). Laser

is used in X-ray production (Pot 2015), Plasma photochemistry (Matthews 2016), annealing (Horiuchi 2017). A glass material $35\text{SrO}-20\text{TiO}_2-45\text{SiO}_2$ (STS45) was thermally treated at 940°C . It possesses the crystalline phase and exhibited optical transparency with second-order nonlinear coefficients of d_{31} and d_{33} were determined as 1.7 pm V^{-1} and 9.6 pm V^{-1} , respectively, at the fundamental wavelength of $1.064\text{ }\mu\text{m}$ (Horiuchi 2017). A non-contact optical scheme for measuring the temperature of a gas was discussed an optical-frequency comb thermometer was developed whereby temperature is determined by the rotational constant of a molecule (Horiuchi 2017). 3D nonlinear optical images of lasers were captured in chiral nematic liquid crystals (Ackerman 2017). Optical fiber communication has been developed by optical fibers embedded with SONLO Crystals (Horiuchi 2017).

Photonic NLO crystals are used in supercontinuum generation (Oh 2014), optical modulators (Mork 2014), soliton laser for torque detection (Song 2014), quantum simulation (Tudela 2015), thermal emitters (Lenert 2014) and Quantum information (Sarah 2016). Three-dimensional photonic crystals were fabricated from fibroin, a silk-derived protein by a biocompatible method (Kim 2012). Photodetectors in UV region was constructed by using Cerium fluoride photoresponsive film (Ieda 2012). High-resolution spectrometer was fabricated based on a planar array of GaP photonic crystal cavities (Gan 2012). By using a photonic crystal cavity with an embedded quantum dot, Chao-Yuan Jin demonstrated the real-time control of the radiative process (Jin 2014). Quantum simulation of many-body systems has been empowered by tune ability of photonic crystals. (Douglas 2015). Non-diffractive light propagation was observed in disordered photonic crystal lattice (Hsieh 2015). The guanine nano crystals present in the skin of the male panther chameleons show the blue shift reflectivity due to the expansion and contraction of the crystal lattice

(Teyssier 2015). Photonic crystals as thermal emitters enhance the operational efficiency in thermo-photovoltaic cells (Inoue 2016). Photonic band gap crystals enhanced coupling of light with nuclei (Haber 2016).TiO₂ simple cubic photonic crystal was fabricated for extreme light trapping (Brian 2017).

1. 7. Overview on Material selection

Sulphamic acid is recommended as a standard material in acid-base titrimetry (Butler 1938, Bishop 1967, Bishop 1973). Sulphamic acid was used as a precursor to synthesize organic sulfate steroid crystals (Joseph 1966). It succeeded benzoic acid, hydrochloric acid and sodium carbonate by its purity, better thermal stability and hygroscopicity. It was purified and recrystallized in water (Bishop 1967). It can also be used in household cleaning products, herbicides, and flame retardants in the form of ammonium sulphamate (Metzger 2000, Yoshikubo 2000). Alkylated Sulphamic acid was then used as artificial sweeteners, therapeutic compounds in antibiotics, HIV inhibitors and anti-cancer drugs (Benson 1980, Winum 2005, Spillane 2014). Sulfamate ions are potential linkers in coordination chemistry (Benson G.A. 1980) due to its strong affinity towards metal ions.

The crystalline structure of Sulphamic acid was determined by many researchers Jaeger F. M. (1926), Brown C. J. (1940), Kanda F. A. (1951), Osaki K (1955) and Jat (2013)

Unit Cell	a	b	c	Space group
Jaeger (1926)	1.006	1	1.146	Not identified
Brown (1940)	8.06	8.05	9.22	Not identified
Kanda (1951)	8.100	8.049	9.228	Orthorhombic
Osaki (1955)	8.006	8.115	9.255	Pcab
Jat (2013).	8.0943	8.0667	9.2589	Not identified

It is handy, low risky and highly stable in crystalline state. Its aqueous solution can dissolve iron oxides. It is compatible with steels (Rehim 2016). These features make it suitable for synthesizing new materials by mixing it with other acids in aqueous solution. Sulphamic acid crystallized as zwitterionic molecule ($\text{NH}_3^+\text{SO}_3^-$) of a distorted tetrahedral in the solid state form but it is a strong monobasic acid in aqueous solution with $\text{H}_2\text{N-SO}_2\text{-OH}$ structure (Kanda 1951). In the zwitterionic form, the bond angles of N-S-O and O-S-O are deviated from normal tetrahedral value due to repulsive/attractive forces among negatively charged oxygen atoms and positively charged ammonia ion. The strong lattice force due to $-\text{NH}_2$ bond accounts to its melting point is 206° higher than other sulfonic acids. Sulphamic acid single crystal was irradiated and proved that the hyperfine couplings in free radical $\text{SO}_3^- \text{-NH}_2^+$ depend on temperature (Rowlands 1962). Hyperfine interaction in sulphamic acid single crystal grown from aqueous solution was examined through electron spin resonance spectrum and also irradiated sulphamic acid crystal with ^{60}Co γ rays at ambient temperature (Atherton 1966). The proton structure in the vicinity of SO_3^- centre was examined through proton ENDOR spectrum (Atherton 1987). Good optical homogeneity Sulphamic acid crystal was grown in aqueous solution by slow solvent evaporation technique and its nucleation and kinetics were studied (Jat 2013). The solubility for various temperature and corresponding saturation temperature and nucleation temperature were calculated. Sulphamic acid was neutralized with potassium hydroxide (Brown 1940) and Potassium sulphamate ($\text{NH}_2\text{SO}_3\text{K}$) crystal was grown in aqueous solution by slow solvent evaporation technique. ($\text{NH}_2\text{SO}_3\text{K}$) has ionic structure with orthorhombic crystalline axes $a = 8.32 \text{ \AA}$, $b = 8.28 \text{ \AA}$ and $c = 5.90 \text{ \AA}$ and space group P_{bma} . It has hydrogen bond with nitrogen only, not with oxygen. Similarly Sodium, Cadmium and Silver

cyclohexylsulphamates were crystallized in aqueous solution (Audreith 1942). Metal sulfamates synthesized by mixing sulphamic acids with metal carbonate/oxide salts are useful in electroplating (Barret 1954) due to its high solubility and zwitterionic nature. Sodium hydroxide and Calcium hydroxide were separately mixed with cyclohexylsulfamic acid in aqueous solution and allowed for slow evaporation. Sodium and Calcium salts of cyclohexylsulfamic acid were crystallized respectively (Birston 1968). To adjust the pH values during the precipitation of metal sulphates, sulphamic acid was mixed in homogeneous solution (Cartwright 1962). Sulphamato based metal halogeno complexes of trivalent rhodium, iridium, ruthenium and osmium, palladium and platinum by mixing metal-halogeno complexes with aqueous sulphamic acid solution. The sulphamato ligand binds with metal ions via the nitrogen atom rather than oxygen (Griffith 1973). Some metal sulphonate salts were precipitated after drying neutral solution containing sulphonic acids. Their spin-lattice relaxation times were compared with pure sulphamic acid by their NMR spectrum (Ratcliffe 1981).

The kinetics in reaction of sulphamic acid with nitrous acid (Hughes 1967) and nitric acid (Hughes 1977a) was studied. Energetically active nitramino substituted compounds are intense fascination of scientists and technologists due to their potential importance to prepare sensitive/insensitive materials in Defense laboratories (Duddu, 2010, Singh 2007).

$\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) is a tectonic crystal charted path to discover more DUV NLO crystals (Chen 2009). Major problems identified apically with KBBF crystal are toxic beryllium content, hard growth habit and cost effective high temperature solution growth techniques (Li 2010, Wang 2013). The incorporation of fluoride ion into borates and carbonates is accepted for structural distortion (Li 2014), vanishing

scattering centers (Fang 2013), aligning asymmetric unit (Li 2010), photo-responsive (Ieda 2012) optical responsive (Yu 2012), blue shift effect in UV region (Zou 2013), moderate birefringence (Wang 2013) and large SHG response (Yang 2015). Fluorine assisted cation coordinates dominate on the alignment of anionic groups which are pushed to make noncentrosymmetric space group in BaMBO₃F crystals (Li 2010).

Phosphoric acid influences the structural and optical behaviors of many organic and inorganic compounds. Phosphoric acid acts as a good structural modulator in bio-proteins (Rezabkova, 2012) and some amino acids (Ewa 1999) also. Phosphorylation enhances the thermo-chemical stability and electro-optic behaviors of some amino acids (Yokotani, 1989), (Smolin, 2003). Phosphorylated tyrosine crystal plays vital role in cellular communication (Lim 2010, Jin 2012). Phosphorylation is an on/off switch for 5-hydroxyconiferaldehyde O-methyl transferase activity in poplar monolignol biosynthesis (Wang 2015).

Lactic acid known as milk acid where optically active isomers namely L(+)-lactic acid, and D(-)-lactic acid could form based on a chiral carbon atom attached with a hydroxyl group, and a carboxylic and a methyl groups are included (Narayanan 2004). Microionized bone particulates could dissolve in lactic acid and directly generate calcium and phosphate containing crystals (Bulysheva 2018). It enhances the spontaneous polarization of ferroelectric crystalline molecules (Otterholm 1987). It provides the chiral lactate ion which reveals peculiar ferroelectric, antiferroelectric orders and V-shaped electro-optic switching properties in liquid crystals (Wu 2005, Senthil 2008). L-lactic acid succeeds chiral precursor material (S)-2-octanol due to its low price and more stabilizing nature in thermal and chemical properties.

Feasible method of mixing of various salts in solvents alleviates the synthesis of new crystalline materials (Ghazaryan 2010). Mandelic acid is mixed with water and its optical rotation in aqueous solution was studied (Levene 1929). Optical lattice modes of mixed crystal system were studied (Lucovsky 1967). Mixed crystal system of $\text{CdSe}_y\text{S}_{1-y}$ was modelled for optically phonons (Verleur 1967). Infrared absorption was induced by impurities in mixed alkali halide crystals (Takeno 1967). Raman scattering was studied from mixed crystal system of $(\text{Ca}_x\text{Sr}_{1-x})\text{F}_2$ and $(\text{Sr}_x\text{Ba}_{1-x})\text{F}_2$ (Chang 1966). Lithium Carbonate was added with Sulphamic acid in aqueous solution to prepare the Lithium sulphamate (Bnoit 1988). Manganese, Copper and Nickel metal ions were doped with sulphamic acid by mixing their respective metal sulphate salts with aqueous sulphamic acid solution (Ramesh Babu 2010). Its aqueous solution makes cystine (Rehim 2016) and Tryptophan (Fatah 2016) as good corrosion inhibitors. The super acidic-ionic liquids (Dupont 2016) have been recently prepared by mixing the N-alkylated sulphamic acid with Bistriflimic acid. Recently Ce^{3+} doped sulphamic acid NLO single crystals by unidirectional method (Brahmaji 2017). Its UV cut-off wavelength is measured as 340 nm and its SHG efficiency is 3.5 times that of KDP. Its direct band gap energy is calculated as 4.6 eV. Tb^{3+} doped sulphamic acid single crystals have been grown by slow solvent evaporation technique and Sankaranarayanan -Ramasamy Method (Brahmaji 2018). It is highly transparent in UV region with low cut off wavelength 259 nm. Its SHG efficiency is 3.6 times that of KDP. Its direct band gap energy is calculated as 4.2 eV.

1. 8. SCOPE OF THE THESIS

Feasible method of mixing of various salts in solvents alleviates the synthesis of new crystalline materials. Sulphamic acid mixed crystal system opens up the possibility of harvesting laser energy.

It gives a voice to mix amino sulphonic acid (sulphamic acid) and nitric acid to explore a new hybrid material nitramino sulphonic acid (NASA).

Structural modulator HF inspires to synthesize a new mixed crystal system of hydrofluoric acid and sulphamic acid (FASA).

Structural distorter Phosphoric acid encourages to synthesize a new mixed crystal system of Sulphamic acid mixed Phosphoric acid (SALA).

Optical isomer lactic gains the attention owing to its active chirality, biocompatibility and biodegradability, anti-corrosion, chemical feasibility and pharmaceuticalability and stimulates to synthesize and grow Sulphamic acid mixed L-Lactic acid (SALA).

The grown crystals are characterized by their structural and chemical properties through crystallographic and spectroscopic analysis. The nonlinear optical behaviors of these crystals are also studied.