Chapter - 1

Introduction

Chapter-1: Introduction of Crystal Growth and Non-linear Optics

1. Introduction:

The elegance of crystals has been driving attention for many years. The fascinating colours, varying shapes, transparency, shiny surfaces, etc., all together stimulated the early man's admiration who used crystal as an ornament (Chernov 1984). Crystals are unrenowned pillars of modern technology. Crystal growth is an interdisciplinary subject with great importance in physics, chemistry, materials science, crystallography, mineralogy, etc. The growth of single crystals has a prominent role in the present era of rapid technological and scientific advancements. Due to the increasing demand for technological applications, there has been growing interest in various crystal growth techniques in the past few decades.

Different methods are established to grow suitable crystals according to the desired application because good quality of crystals is needed for a variety of applications. The crystalline property has been found to have applications in such instruments as laser resonators, scintillation detectors, acoustic-optic modulators, piezo-electric sensors, holographic systems, polarizers, thin-film substrates, ion-sensitive electrode membranes, etc. [1-2]. Single crystals play a dynamic role in most of the applications listed above. Consequently, the growth and characterization of single crystals to manufacture devices are significant in both primary and applied science research. The advancement and modification of crystal growth methods to achieve usable products depend heavily on experimental research and technique of trial and error.

Crystal growth is a subject of art and is a part of the phase change phenomenon; thus, three specific categories of crystal growth processes can be described [3].

- Melt Growth (L→S) where liquid-solid phase transitions are involved.
- Solid Growth (S→S) where solid-solid phase transitions are involved.
- Vapour Growth (V→S) where gas-solid phase transitions are involved.

The nature and production of the numerous crystal growth methods of the present day are the consequence of ongoing and productive improvements that have taken place over the last few decades, and the process of modification is still underway. Crystal growth involves prominence on the following three factors [4]: **1.** Nucleation and growth theory, **2.** Crystal synthesis and **3.** Characterization of crystals.

Several authors described competitive nucleation in crystal growth in a detailed manner [4,5]. Gilman [6] has aptly referenced in his book 'The Art and Science of Growing Crystals' as, 'The systematic production of artificial crystals' or it can refer as a new 'Agriculture". It differs from traditional agriculture because its goods are primarily inorganic at present. Still, it has specific characteristics in common with conventional agriculture and aims to have a very comparable impact on society.

There are several well-written books available on subjects such as the foundations of crystal growth [7], the various methods of crystal growth, their hypotheses, their analyses and applications [8-12], and their interpretation of the growth mechanism and related topics have been extensively mentioned in the literature [6, 13-21]. The basic standard theory of these approaches is that the nucleus is formed first and grows into a single crystal by arranging and constructing ions or molecules into complex coordination and bonding. The mechanism functions slowly, and several nucleations are reduced.

Crystal growth mechanisms and the size of the grown crystals vary greatly and are dictated by the characteristics of the material. A variety of methods are used for each type of crystal growth. The model for choosing a specific process relies on the properties of materials such as vapour pressure, melting point, solvent, solubility, decomposition, etc. The growth methods are also highly influenced by their kinematics involved, crystal size and shape requirements, purity, and the nature of the crystal's application.

2. Crystal growth from solution:

One of the most commonly used methods for crystal growth is the formation of crystals from solution. This technique is studied in the culture of crystal growth, next to the technique of melt growth. The most significant advantage of solution growth is that crystals can be formed at temperatures far below their melting points. However, comprehensive inherent knowledge is needed for melt growth techniques, such as melting point, stability in reduced pressure, melting behaviour, phase diagram, and atmosphere, which is unnecessary for solution growth. This technique caters to a multitude of technologically essential crystals. The methods of solution growth can be subdivided widely as follows [9].

1. **Hydrothermal Growth:**

This technique is aqueous solution growth at high temperature and pressure, which apply to materials with minimal solubility under ordinary criteria. The calcite and quartz crystals are produced using this method.

2. **Metallic-Solution Growth:**

This process produces single metallic phase crystals and inorganic compounds that are easily obtained by solidifying saturated metallic solutions. Under high pressure and with the help of transition-metal solutions, diamonds are widely produced. Today, this method is used to grow semiconducting crystals such as GaAs for the industry.

3. **High-Temperature Solution Growth:**

This method is also known as "flux growth". Liquid salts are the only solvents for oxides or solid solutions of oxides, which disintegrate before melting or has very high melting points. In a flux, oxides of fluorides are dissolved, and growth occurs at very low temperatures, often as low as 1000 °C below the solute's melting point. Popular fluxes include KF, PbO, PbF_2, B_2O_3. With this technique, different ferrites and garnets can also be produced.

4. **Low-Temperature Solution Growth:**

For the growth of single crystals, especially when the starting materials are unstable at high temperatures, the low-temperature solution growth is the most extensively used technique that allows the materials to crystallize with prismatic morphology. This approach usually includes the seeded growth from a saturated solution. The driving factor, i.e. the supersaturation, is either accomplished by lowering the temperature or evaporating the solvent. This method is commonly used to grow bulk crystals that are highly soluble and have quite significantly temperature-dependent solubility [22,23].

The solution growth method yields high-quality crystals for a range of applications after many improvements and refinements if required. Crystal growth from solution at room temperature has several benefits over other growth processes as the crystallization rate is slow, giving thermodynamic stability to the process. Since growth is conducted at room temperature, the structural deformities of crystals grown in solution are comparatively low [24]. The solution growth at low temperature can be further subdivided into the following techniques:

1) **Slow Cooling Technique**
2) **Slow Evaporation Technique**
3) **Temperature Gradient Technique**

Slow cooling and slow evaporation methods are identical to each other as far as the basic apparatus is concerned. In this process, the saturated solution is maintained at a certain temperature, and provision is made for the saturated solution to evaporate. Evaporation into the open atmosphere is permitted if the solvent is non-toxic, for example, water. Typical conditions for growth include temperature stabilization of about 0.5 °C and evaporation rate of a few mm^3/h. The technique of evaporation has an advantage; namely, crystals grow at a fixed temperature. However, there is a significant influence on the growth rate due to the inadequacies of the temperature control system. This technique can be used extensively for materials that have a very low-temperature coefficient of solubility. The crystals appear to be less pure than the crystals formed by the slow cooling method; therefore, there are chances that more impurities are found in the crystal faces when the size of the crystal increases.

Undesirable nuclei are formed, and high local supersaturation occurs due to the evaporation of the solvent. After evaporation, tiny crystals are formed at the surface of the liquid and on the vessel walls. Such grown crystals around the vessel wall fall into the solution and obstruct further crystal growth. Another drawback is regulating the evaporation rate, which is variable and can influence the crystal attributes. Despite all these demerits, this is an efficient and suitable technique for growing large size single crystals. Crystals of Ammonium Dihydrogen Phosphate (ADP) and Potassium Dihydrogen Phosphate (KDP) are grown using three methods **1.** Solution Growth [25] **2.** Sankaranarayanan-Ramasamy (S-R) process [26] **3.** Gel Growth [27].

We have used this method to grow pure and doped KDP crystals. Pure KDP crystals are grown by weighing molecular weight percentage and dissolving it in deionized water. Then the beaker was kept on a magnetic stirrer and was continuously stirred for 3-4 hours until a homogenous and saturated solution is obtained. The saturated solution of KDP is filtered into another glass beaker and covered with a perforated sheet to allow gradual evaporation of the solvent. The beaker is kept in a clean place and in a dust-free room with little or no temperature variation and a monitored ambience. Figure 1 depicts the schematic diagram of this process. For amino acid doped KDP crystals, required weight percent dopants are added to the KDP solution, and the same procedure is repeated.

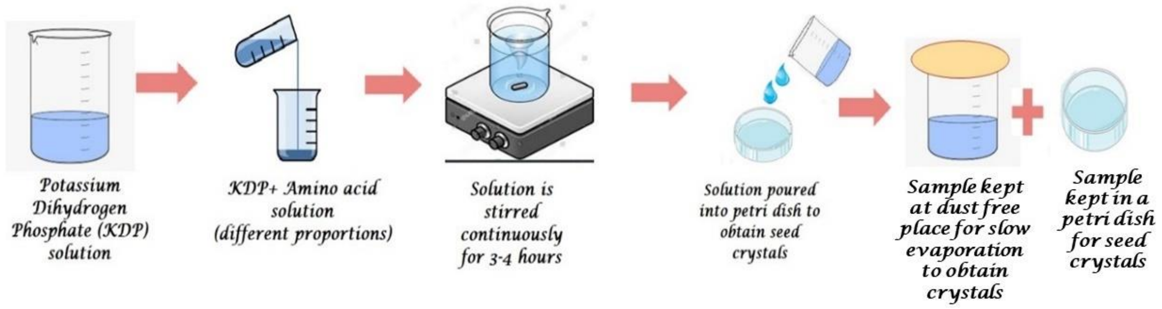

Figure 1. Crystal growth process

3. Expression for supersaturation:

The methods for growing crystals from solutions are generally dependent on the solubility of a substance. This solubility of the substance depends on the thermodynamic parameters of the process, such as temperature, pressure and solvent concentration. In most instances, solubility temperature dependence is used. For crystallization to take place, a state of supersaturation is essential. The degree of supersaturation can be expressed in one of the simple ways through the following relation:

$$S = C / C^{*} \tag{1}$$

where, C=Concentration of the solution

C^{*}=Equilibrium saturation concentration at the same temperature

Thus, the values of S denotes three separate saturation states; respectively,

1. $S = 1$ indicates a saturated solution
2. $S < 1$ indicates an undersaturated solution
3. $S > 1$ indicates a supersaturated solution

The concentration driving force C and relative supersaturation σ are other familiar expressions of supersaturation, described by [28]:

$$\Delta C = C - C^{*} \text{ and } \sigma = \frac{\Delta C}{C^{*}} \tag{2}$$

It is required to analyze and research the temperature concentration (T-C) diagram for most solution growth techniques [29].

3.1 Solubility curve:

It is easier to calculate supersaturation when the corresponding equilibrium saturation concentration and the concentration of solution measured at a given temperature are identified. Meirs and Isac [30] conducted substantial research on the relationship between spontaneous crystallization and supersaturation, and the outcomes can be depicted as seen in figure 2.

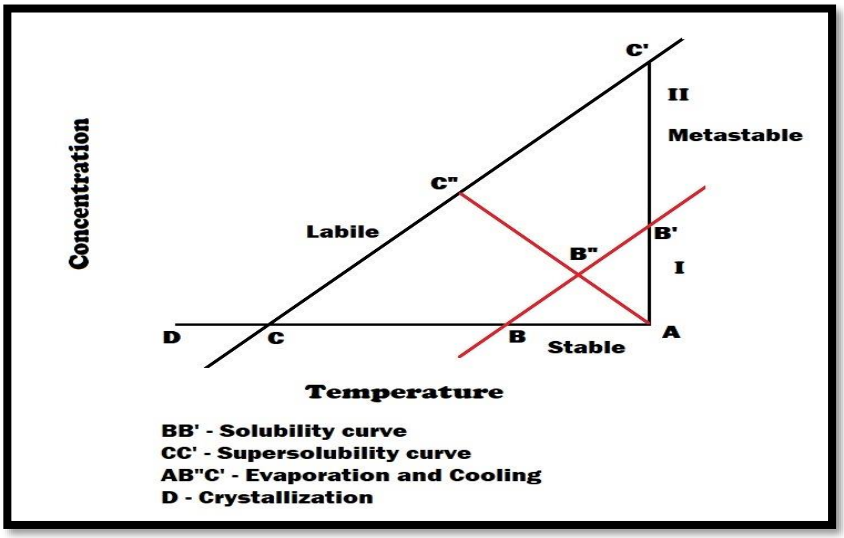

Figure 2. Solubility curve showing various saturation levels

The lower continuous line is the standard curve of solubility for the salt involved. The upper split curve, commonly referred to as the super solubility curve, describes the temperature and concentration at which spontaneous crystallization occurs. This curve is not well described as the solubility curve, and its placement in the diagram depends on the degree of the solution's agitation. This diagram is divided into three zones, namely, **1. "The stable zone",** also known as the under-saturated zone, in this zone, crystallization is not possible **2. "The second zone"** is also known as the metastable zone. It is located between the solubility and super solubility curves, where spontaneous crystallization is unlikely to occur **3.** "**The third zone"** is also known as the unstable zone; there is more probability of spontaneous crystallization in this zone. It is also known as the supersaturation zone.

The crystal growth will occur on a crystal seed if a crystal seed is directly introduced in the metastable solution. Point A in figure 2 represents the solution's concentration and temperature, which is cooled without the solvent's loss and is depicted by line ABC. Until conditions represented by point C are met, spontaneous crystallization cannot occur. Crystallization can be spontaneous at this stage or caused by seeding, mechanical shock, or disturbance. Before crystallization can be induced, further cooling to some point D may be explicitly required with highly soluble substances, for example, sodium thiosulfate.

Supersaturation can also arise from the evaporation of the solvent from the solution. Line AB'C' would be an operation performed at a constant temperature. Usually, the surface on which evaporation occurs is supersaturated to a greater extent than most of the solution because penetration into the labile zone outside the super solubility curve seldom occurs.

Eventually, crystals that emerge on this surface sink into the solution and seed it. A mixture of cooling and evaporation is also followed, as described in the figure by the line AB”C’. This has been discussed elaborately by Chernov in his book [29].

3.2 Selection of solvent:

A homogeneous mixture of a solute and a solvent is called a solution. The component present in a smaller quantity is the solute. There may be various solvents for a given solute. A suitable solvent is needed for solution growth besides high purity starting materials. The solvent must be selected by taking the following considerations into account:

- Low viscosity
- Low corrosion
- Good solubility gradient
- Low volatility
- High solubility

4. Non-linear Optics (NLO):

Optics is referred to as the study of light. It is classified into various scientific methods of treatment like quantum optics, physical optics, and geometrical optics. Some new fields like magneto-optics and electro-optics have been developed recently because of the evolution of the optics branch. New extended areas of optics are accessible such as singular optics, non-linear optics, mathematical optics, non-imagining optics. Bloembergen and Perhan [31] predicted harmonic light waves’ presence at the boundary of a non-linear dielectric layer. However, in 1961, Franken observed the first experimental proof of the second harmonic generation (SHG) of the fundamental pump laser beam in quartz crystals [32].

The observation of other non-linear optical effects is accompanied by the discovery of SHG in quartz. Due to this, there has been an enhancement in crystal growth research to produce several new crystals having promising non-linear optical (NLO) properties. Due to the broad applications of NLO in the field of optical communication, laser technology and data storage have become attractive and popular fields. The study of the interaction of strong electromagnetic (EM) fields with materials to create modified fields that are different from the input field in frequency, phase, amplitude, or other characteristics of the incident field is broadly considered by NLO.

When light is propagated through a crystalline solid with non-centro symmetry, a light at the second harmonics of the applied frequency is generated. Such significant non-linear property of crystals is called Second Harmonic Generation (SHG). This phenomenon and the materials in which it occurs have been the subject of extensive study. [33].

4.1 Non-linear optical phenomena:

The non-linear effect is explained by the way a beam of light propagates through a solid. The atom's nuclei and electrons form electric dipoles in the solid material. When the EM radiation interacts with the dipoles, these dipoles start oscillating. As a result, these dipoles act as a source of EM radiation by the classical laws of electromagnetism. The dipoles emit radiation of the same frequency as the incident radiation depending on the vibration amplitude, whether low or insignificant. The relation between irradiance and amplitude of vibration becomes non-linear as the intensity of an incident radiation increases. As a result, the frequency of radiation released by the oscillating dipoles results in the production of harmonics. When the incident intensity is increased, the frequency-doubling or SHG and higher-order frequency effects arise.

The induced polarization in a non-linear medium is a non-linear function of the applied field. A medium exhibiting SHG is made up of molecules arranged in the crystal with asymmetric charge distributions so that the entire crystal retains a polar orientation. The induced polarization is directly proportional to very low electrical fields [34]. By considering the response of the dielectric material at the atomic level to the electric fields of an intense light beam, non-linear optical effects are studied. For example, a dielectric medium held in an electric field gets polarized if the medium transitions at the field frequency. As a result, each constituent molecule behaves as a dipole having dipole moment P_i.

The dipole moment vector per unit volume P is denoted by

$$P = \Sigma_i P_i \tag{3}$$

where, Σ_i is the summation for the dipoles in unit volume.

The medium and field strength properties become deciding factors for the orientation effect of the external field observed on the molecular dipoles. It can be written as;

$$P = \varepsilon_o \chi E \tag{4}$$

where, ε_o is the permittivity of free space, χ is the linear susceptibility of the material, and E is the electric field vector.

The amplitude of the dipoles does not accurately represent the same sinusoidal electric field when the applied electric field strength is large enough and equal to the inter-atomic field. Indeed, the distorted reradiated wave is generated, which contains the induced polarization given by,

$$P = \varepsilon_o\chi^{(1)} E + \varepsilon_o\chi^{(2)} E^2 + \varepsilon_o\chi^{(3)} E^3 + \ldots\ldots\ldots\ldots. \quad (5)$$

where, $\chi^{(1)}$ is first-order linear susceptibility responsible for the medium's linear optical properties, such as refractive index, birefringence, absorption, and dispersion. $\chi^{(2)}$ and $\chi^{(3)}$ are second and third-order non-linear susceptibilities, and their magnitude reduces as their order increases (10^{-8}:10^{-16} and so on).

The $\chi^{(2)}$ term gives rise to frequency mixing, SHG, and parametric generation. The $\chi^{(3)}$ term gives rise to optical bi-stability, phase conjugation, third harmonic generation (THG), and stimulated Raman scattering. The simplest way to create new frequencies not accessible from existing laser sources is to conduct lower-order non-linear responses. Crystals cannot produce the second order susceptibility $\chi^{(2)}$ with a centro-symmetric structure (inversion symmetry), and as such, the media does not possess the familiar SHG; however, these third order non-linear effects are probable and effective in such media.

There is a two-stage process involved in generating second harmonic waves from the incident wave of frequency (ω_1). First, at the second harmonic frequency ($2\omega_1$), a polarization wave is produced, and the phase velocity, and wavelength of this wave, is determined by the refractive index of the fundamental wave (n_1), i.e., $\lambda_p = c/(2\nu_1 n_1)$. The transfer of energy from polarization wave to EM wave at frequency $2\omega_1$ is the next step. The EM whose wavelength and phase velocity are determined by the refractive index of the harmonic wave (n_2), i.e., $\lambda_p = c/(2\nu_1 n_2)$. The phase velocities of the fundamental and second harmonic waves must be equal to achieve efficient frequency conversion and sustainable growth of the SHG. This prompts the phase-matching condition and is also written as $n_1 = n_2$ here n_1, and n_2 are refractive indices for fundamental and second harmonic waves.

The birefringence of the medium in the optical region gives rise to this phase mismatch (Δk) between polarization and EM waves. It is given by,

$$\Delta k = 4n\,(n_1 - n_2)/\,\lambda_1 \quad (6)$$

The fact is that by using the medium's normal birefringence to achieve zero mismatch, it is possible to offset the dispersion of phase velocities of both waves in the non-linear optical medium. Different approaches for achieving zero mismatches are available, such as index phase matching, angular phase matching, and temperature. It is often preferable to achieve $\Delta k = 0$ by adjusting the medium's birefringence in index phase matching by selecting a suitable polarization and propagation direction. It is possible to modify the birefringence of the extraordinary wave by changing the temperature of the medium through a temperature tuning controller since its index of refraction is temperature dependent. In the case of angle tuning, the extraordinary wave's refractive index varies and equals to the refractive index of the fundamental wave as the angle between the wave normal and optic axis is changed, resulting in precise phase matching.

In addition, if the direction, i.e., phase-matched direction, coincides with one of the optical axes, then it is known as 'non-critical phase-matching'. However, if the phase-matched direction does not coincide with the optical axis, it is called 'critical phase matching'. The crystals have to be appropriately phase-matched to enhance the efficiency of frequency doubling [35,36]. The phase matching in SHG is categorized into type I and type II, depending on the possible orientation of the linear polarization of the incident radiation. When two input waves have the same polarization of frequency (ω_1) and merge to form a wave of frequency ($2\omega_1$), it is called phase matching type-I, $2n_e^{\omega} = n_o^{2\omega}$. If the same waves of frequency (ω_1) are orthogonal to each other, then it is called phase matching type-II, $n_o^{\omega} + n_e^{\omega} = 2n_o^{2\omega}$. The crystal length (l), phase mismatch (Δk), and power density are the factors on which conversion efficiency depends. If the crystal has a fixed length, then the SHG relies significantly on the phase mismatch (Δk). Higher conversion efficiency is typically associated with higher power density, more extended crystals, large non-linear coefficients, and low phase mismatching. Also, the input power density needs to be lower than the damage threshold of the crystal. For a specific application, table 1 lists the laser and crystal parameters for selecting an NLO crystal.

Table 1. The schemes for classifying crystal growth techniques.

Laser Parameters	Crystal Parameters
NLO processes	Type of phase matching
Divergence	Acceptance angle
Power, Repetition rate	Damage threshold
Bandwidth	Spectral acceptance
Pulse width	Group velocity mismatching
Environment	Moisture, Temperature acceptance
Beam size	Crystal size, walk-of angle

4.2 Non-linear optical materials:

Most organic and inorganic materials are good subjects for study as they are highly polarizable. The fact is that photons are proficient in processing information at the speed of light, due to which non-linear materials would be core elements of future photonic technology. Earlier studies focused on inorganic materials such as Quartz, Lithium Niobate ($LiNbO_3$), KDP, and semiconductors such as Selenium, Tellurium, and Cadmium Sulphide. In 1965, Rentzepis and Poa discovered SHG in organic material ‘benzyprene’ [37].

The Kurtz and Perry powder SHG method [38] was introduced at the end of the 1960s. In this technique, with the help of a laser, the powder sample is irradiated, and the light which is scattered after irradiation is accumulated. With the help of appropriate filters, it is analyzed for its harmonic content. It was possible to do a rapid, qualitative screening for the second order NLO effect for the first time. After that, the stage was set for the rapid introduction of new inorganic and organic materials. Inorganic materials are substantially more developed in their application for second order NLO than organics. Also, most inorganic materials are used as commercial materials, particularly for high power use. Organic materials, however, are perceived to be more diverse structurally. It is therefore thought that it has more long-term promise than inorganic. Organic solids have a massive range of attractive properties that are almost continuously tunable. A non-linear material should have the following features for optical applications [34]:

- A broad optical transparency domain,
- High laser damage threshold,
- A prominent non-linear figure of merit for frequency conversion,
- Readily available in large single crystals,
- Comprehensive phase matchable angle,

- Ability to process into crystals, thin films, etc.
- High mechanical strength and thermal stability,
- Fast optical response time,
- Ease of fabrication
- Non-toxicity and good environmental stability

Two factors decide the existence or absence of efficient SHG for displaying SHG in materials. Firstly, the most fundamental factor is that the material should crystallize with a non centro-symmetric crystal structure. Secondly, crystals should possess phase-matching properties for optimum SHG performance (i.e., in the crystal, the propagation speed of the fundamental and harmonic waves should be equal). For scientists, the quest for novel crystals with NLO properties is still a challenge. For NLO crystal, the following parameters are critically important [39,40]:

- Non-linear optical coefficient, χ_{ijk}
- Birefringence
- Absorption edge on the UV side for the UV crystals
- Damage threshold
- Optical homogeneity
- Physio-chemical stability and mechanical properties

A systematic discussion of non-linear optics is avoided since several scholars have discussed various aspects of non-linear optics in detail. It has also been dealt with in-depth in some recent books on NLO [41-44].

4.2.1 Inorganic non-linear optical materials:

Inorganic crystals are ionically bonded, and due to their high degree of chemical inertness and high melting point, they are easier to synthesize. Lithium Niobate ($LiNbO_3$), Potassium Niobate ($KNbO_3$), Potassium Titanly Phosphate (KTP), Ammonium Dihydrogen Phosphate (ADP, NH_4PO_4), KDP, Beta Barium Borate (β-BaB_2O_4), etc. are some of the most valuable crystals discovered so far. Many of these materials have been used extensively to provide coherent laser radiation with high-frequency conversion efficiency and commercial frequency doublers, mixers, and parametric generators.

4.2.2 Organic non-linear optical materials:

Due to their large nonlinearity, the focus was mainly on new NLO organic materials. Due to NLO properties of large organic polymers and molecules, they have become subject of substantial theoretical and experimental investigations during the past two decades. The following list shows the advantages of organic non-linear optical materials [34]:

- High second order non-linear optical efficiency
- Much more excellent resistance to damage in the laser beam
- They are birefringent (facilitates phase matching)
- Possible to chemically “engineer” molecular properties

Organic material is called perfect when it has a very low absorption edge cut-off (to allow access into the UV), a high efficiency, a high damage threshold and favourable crystal growth properties. Compared to inorganic materials, the improvement in nonlinearity is due to the presence of π-electrons in organic materials. For various applications such as SHG, electro-optic modulation, frequency mixing, optical bi-stability, optical parametric oscillation, etc., organic NLO crystals have emerged as attractive and essential candidates. Organic NLO materials’ dominance comes from their adaptability and ability to modify them for specific end-use. The organic conjugated molecules, which have an e^- acceptor group at one end and a donor group at the opposite end, give rise to large second order optical nonlinearity. Also, we can say that a significant amount of second order nonlinearity originates from such organic conjugated molecules. Some of the π-conjugated systems will be benzene, benzylidene, biphenyl, polyenes, etc. There are e^- acceptor and donor groups which can be affixed to a π-conjugated system like donor groups: $NHCH_3$, NHR, NH_2, F, Cl, CH_3, Br, OH, $NHCOCH_3$, etc. and acceptor groups: NO, CN, COOH, NO_2, $COOCONH_2$, CONHR, $CONR_2$, CHO, etc. [34].

There are several organic NLO crystals such as 2-[2-(4-Methoxy-Phenyl) Vinyl]-1-Methyl-Pyridinium tetrafluoroborate [45], 4-Ethoxybenzaldehyde-N-methyl-4-Stilbazolium Tosylate (EBST) [46], 4-dimethylamino-N-methyl-4-Stilbazolium Tosylate (DAST) [47], 4-Nitrophenol urea [48], etc. Also, Basu [49] wrote a book on a review of organic NLO materials, and detailed books on organic NLO materials are available [50,51].

4.2.3 Semi-Organic non-linear optical materials:

Some of the demerits of aromatic crystals are low hardness, poor physiochemical stability and cleavage tendency which can hinder the device application. Therefore, a new class of NLO crystals-metal organic or semi-organic complex crystals was introduced and developed to preserve the merits and resolve the shortcomings of organic materials [52]. Due to their vast nonlinearity, recently, attention is concentrated on metal complexes of organic compounds [53]. Combining the excellent physical properties of inorganic molecules with the high non-linear optical coefficients of organic molecules has been overwhelmingly effective in recent years. Therefore, recent research focuses on semi-organic NLO materials because of their large nonlinearity, low angular sensitivity, high resistance to laser-induced damage and good mechanical hardness [54-56].

The π-conjugated network (in an organic system with wide nonlinearity) has exceptional absorption in the entire visible region. Therefore, organic materials are less explicitly delocalized and are more transparent for SHG in the blue-near UV region. There are some amino acids based semi-organic non-linear crystals such as L-Serine Methyl Ester Hydrochloride [57], L-Threoninium Cadmium Chloride [58], L-phenylalanine Trichloroacetate [59]. Kar [60] and Fleck [61] have published two different articles on amino acid-based semi-organic NLO crystals.

5. Significance and applications of NLO materials:

For diverse applications, materials with high non-linear optical characteristics are presently interested in technological and scientific fields. A broad variety of non-linear optical materials currently exists with various wavelength, damage thresholds and optical characteristics. To meet all requirements such as high damage threshold, fast response and wide transparency range coupled with adaptability, processing ability and the ability to amalgamate with other materials, the focus should be on developing materials that meet the described aspect. There are many applications of NLO materials; however, the major use is in sum-frequency generation, frequency conversion, differential frequency generation, frequency doubling, optical parametric generation, etc., for different optical applications. Gamire [62] has carried out a definitive study on using non-linear optics in everyday life, depicted in figure 3.

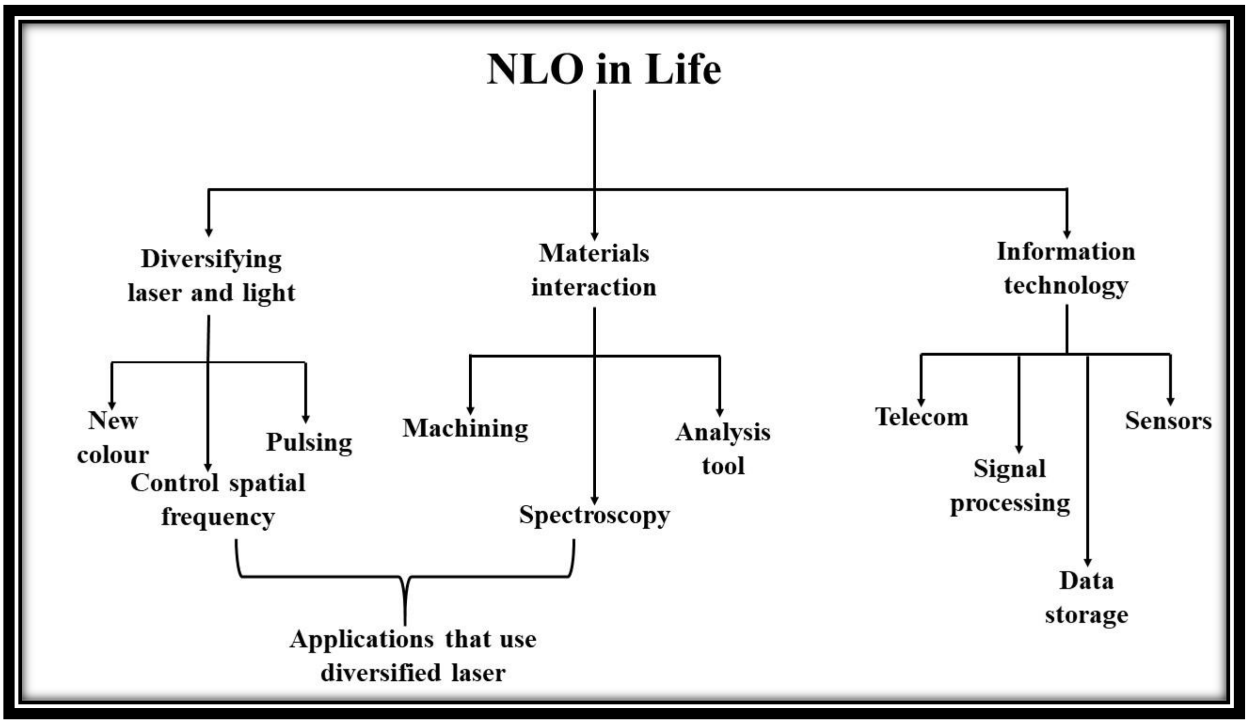

Figure 3. Schematic diagram of NLO crystals in daily life.

Gamire [62] has provided a broad-angle application of NLO materials in this excellent review, due to which it has become an interdisciplinary field. In addition, Sutherland [63] has also covered various NLO material applications like electro-optical effect, optical limiting, multi-photon absorption, optical switching, etc. According to the market overview, the global photonic crystal market size was estimated at $34199 million in 2015 and forecasted to hit $60230 million in 2022 [64].

6. Potassium Dihydrogen Phosphate (KDP): A NLO crystal:

The crystal structure of the KDP (KH_2PO_4) with its molecular position in the unit cell is shown in figure 4. KDP has a tetragonal structure with $1\bar{4}2d$ phase group and reported lattice parameters are a=b= 7.44 Å and c= 6.97 Å [65]. Each PO_4 tetrahedron is bound to four others in KH_2PO_4 by hydrogen bonds (H-bonds) from each of its corners. This forms a continuous anionic network in the crystal. The growth of KDP from melt decomposes at high temperatures. KDP has moderate solubility in water (appropriate solubility gradient). KDP crystals are grown from solution either by slow evaporation (at room temperature) or by slow cooling of the saturated solution. At room temperature, KDP crystallizes in the tetragonal system. There is a phase transition of KDP below 123 K, and the crystal becomes ferroelectric, having orthorhombic symmetry. In an orthorhombic phase of KDP, the polar axis lies along the direction of the c-axis. For hydrogen-bonded ferroelectrics, KDP is known to be a standard substance. KDP shows significant resistance laser damage (a mechanical form that occurs with very high power densities) and change in refractive index (which results from low continuous wave powers) since both effects have been observed.

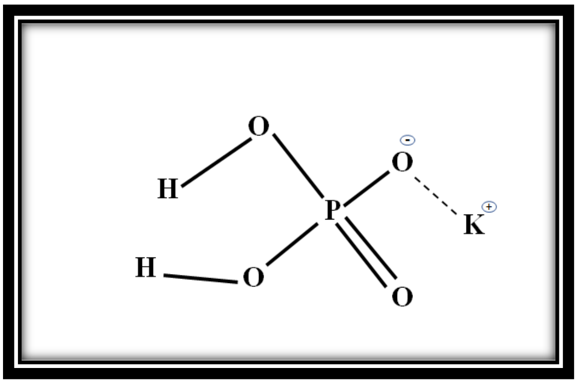

Figure 4. Crystal structure of Potassium Dihydrogen Phosphate (KDP)

KDP single crystals below 123 K shows spontaneous polarization, which has attracted many researchers to analyze the promising coupled properties such as dielectric characteristics, electro-optic behaviour and piezo-electric. KDP is a non-linear ferroelectric crystal, and it is widely used for electro-optical applications like SHG, Q-switching, electro-optic modulation, etc.

Table 2. Non-linear optical parameters of Potassium Dihydrogen Phosphate (KDP)

Sr.No.	Parameters of KDP	
1	Crystal structure	Tetragonal
2	Lattice parameters	a = b= 7.44 Å and c = 6.97Å
3	Space group	$1\bar{4}2d$
4	Density (gm/cm^3)	2.33
5	Refractive index (at l=1064 nm)	$n_o = 1.4938$, $n_e = 1.4599$
6	Electro-optic coefficient (r^{63}, pm/V)	$r^{63} = 10.3$ and $r^{41} = 8.8$
7	Absorption coefficient (cm^{-1})	0.07
8	Transparency range (mm)	0.2 - 1.5
9	Nonlinear coefficient (pm/V)	$d^{36} = 0.44$
10	Wavelength range (nm)	200-1500

7. Impurities importance in KDP:

If there are slight traces of impurities in the system, then the nucleation rate of a solution or melt can be significantly influenced. In multicomponent processes, crystallization of solution often occurs since certain impurities are even in the purest form. Impurities could be present in the form of a solid and in a dissolved state. The solvent itself represents a colossal impurity when crystallization occurs from the solution [66-67]. The solvent can also interact with the solute, and this process may not be distinct as the solute must diffuse to the growing crystal face. It may involve the solution solvation of ions or molecules at the active growth sites and in the adsorbed layer. Therefore, the solvent may have a substantial effect on the method of crystallization. Either homogeneously or heterogeneously or by secondary nucleation, crystal nucleation takes place. Due to materials that are in contact with the solution, heterogeneous nucleation occurs; however, homogeneous nucleation happens either randomly as induced or spontaneously. The presence of impurities significantly affects the nucleation behaviour of a solute.

In an aqueous solution, the presence of small quantities of colloidal substances (for example, gelatin) can suppress nucleation, and specific surface-active agents also exert inhibitory effects. Some minute cracks and interstice can serve as a nucleation catalyst if they are present on the surface of the nucleation cell. Supersaturation is required to form crystals from their solution; however, the supersaturation reduces if there is any presence of foreign crystal [68]. Some impurities can enhance the nucleation, and some can also suppress the nucleation, while others may apply a profoundly specific exertion. Many scholars address the mechanism of the impurity effect, the kinetics of phase transition [69-73]. Impurities can alter the kinetics of the salt crystallization due to the facet adsorption of growing crystals due to the alternation of the actual solution supersaturation due to the modification of the crystal-solution boundary layer structure. The predominance of either of the impurity as mentioned above processes in the crystallization process can only be proven by considering the properties of the impurity introduced to the solution, its interaction with the solvent, it's potential to produce a new compound with the given system, its state and concentration in one or another phase.

8. Significance of doping amino acids in KDP:

Amino acids are called bi-functional organic molecules because they contain an amine (-NH_2) group and carboxyl group (-COOH) also, they have a de-protonated carboxylic acid group (COO^-) and a protonated amino group (NH_3^+) in a solid state. Zwitterionic nature in amino acids exhibits unique physical and chemical properties, making them ideal for NLO applications [74].

- Amino acids are potential candidates for an optical second harmonic generation because they contain chiral carbon atoms and crystallizes in non-centro symmetric space groups.
- Zwitter ionic nature of amino acids, which facilitates crystal hardness.
- Wide transparency ranges in the visible and UV spectral regions because of the absence of strongly conjugated bonds in amino acids.
- The amino acid has well-defined size, charge and hydrophobicity.

9. Recent literature survey:

Potassium Dihydrogen Phosphate (KDP) is part of a vast family of MH_2PO_4 (where M=K, Na, NH_4^+, X=As, P). A vast volume of literature is available on different doping on KDP crystals, and it will be very arduous to include and address each one. Therefore, the present author has reviewed papers conducted only on pure, amino acids, metal ions, and other dopant added KDP crystals in the last few years. KDP is an isomorphous crystal widely used as electro-optic material. It is a negative uniaxial crystal and has a transmission band from ultraviolet to near infrared. First developed as piezo-electric material, KDP and ADP crystals are commonly used for ultrasonic transducers. Its non-linear coefficient, later on, became a reference against other materials for comparison. The first crystals used for the demonstration of phase-matched second harmonic generation are KDP and ADP. These materials display outstanding resistance to laser damage of both the refractive index shift damage that occurs from low continuous wave forces and the mechanical form that occurs with very high-power densities. Also, these materials are simple to grow from an aqueous solution that makes large, high-quality single crystals readily available.

KDP and ADP have a 4-fold symmetry axis taken as the z-axis (optic axis) by strict convention and two mutually orthogonal 2-fold symmetry axes (designated as X and Y axes) that lie in the plane normal to z-axis. KDP is a prototype of a family of crystals with bridging hydrogen bonds, and its physical properties have been extensively studied [75]. The external shape of the crystal or the habit of the crystal is dependent on the different growth rates of different faces of the crystal. One set of faces may be caused to grow faster than the others under a particular crystallization condition, or the formation of one set of faces may be impaired/slowed. In contrast to <001>, KDP crystal typically grows relatively slowly along

<100> under standard pH conditions. Due to the screw dislocation mechanism, growth on the <100> face is observed. This report was verified by showing that elliptical layers with the major axis along <001> and minor axis <100> moving outward across the surface from established growth centres characterized the growth of <100> face of KDP crystals. By the dislocation mechanism, KDP family crystal tends to grow. A non-vanishing point is formed due to the emergence of screw dislocation on a face. It is twisted into a spiral by crystallizing matter attached to the stage. Due to this spiral movement, a dislocation hillock appears and extends over the face and is normal to it as seen in figure 5. This allows the crystal to grow.

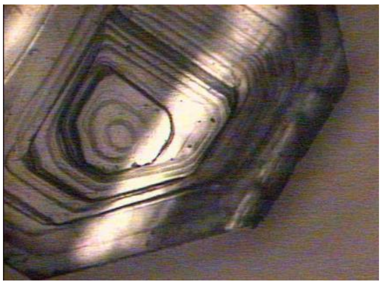

Figure 5. Growth layers and hillock structure of KDP

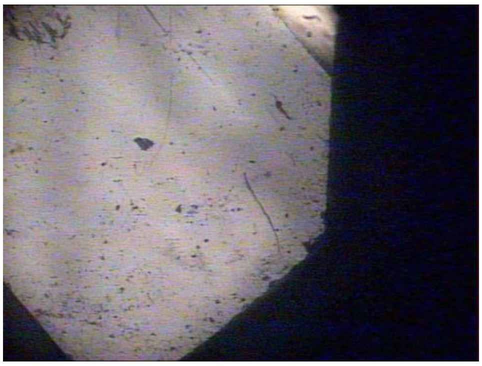

Figure 6. Surface photograph of KDP crystal

Various factors limit normal crystal growth when large crystals are grown. Therefore, technical challenges associated with the need to sustain steady development conditions over a long time are becoming more pronounced. Because of their vast size, the inspection and machining of such crystals become complicated to manufacture optical elements of required characteristics.

For an optical harmonic generation in the visible region, KDP and ADP are effective angle tuned dielectric mediums [76]. To improve the performance of the SHG for KDP crystals, a variety of studies have been undertaken to define potential approaches for improving the efficiency of the transfer of laser radiation by diversifying the structure of KDP and ADP, which are two well-known non-linear optical single crystals [77-79] or developing composite semi-organic non-linear optical crystal [80,81]. Hydrogen bonds such as O-H----- and N-H--O play a vital role in optical nonlinearities of organic, inorganic, and semi-organic crystals [82]. Non-linear optical phenomena such as the generation of higher harmonics and electro-optical effects are directly dependent on hydrogen bonds of the KDP crystal family. Increasing the number of hydrogen bonds and enhancing these bonds' spatial location enables regulating the crystal's non-linear optical characteristics [83-85]. There have been many reports of the inclusion of different amino acids in the KDP crystal structure, due to which the SHG has enhanced [86-89]. Many attempts have been made to integrate organic molecules such as amino acids into the KDP family of crystals. Such molecules are strongly polarizable due to internal charge transfer processes between the donor (COO^-) and acceptor (NH_2^+) groups [90]. While analyzing the effect of amino acids on the electrical properties of KDP single crystals, it is noticed that the electrical properties of KDP either decrease or increase with the change in the amount of concentration of amino acids in it. This occurs due to decreased or increased L-defects, which are primarily induced by the formation of additional hydrogen bonds due to the impurity that hinders the motion of the protons [91].

10. The Objective of the Present Study:

The present study aims to modify the properties of KDP with amino acid doping with different growth techniques. The following is the aim of the present study:

1. Growth and characterization of pure and three different amino acids doped KDP crystals, mainly L-Cysteine (1 mol% and 2 mol%), L-Arginine (1 mol% and 2 mol%) and L-Leucine (1 mol% and 2 mol%).
2. Crystal Growth and characterization of pure and two amino acids doped KDP crystals, L-Cysteine (1 mol% and 2 mol%), L-Arginine (1 mol% and 2 mol%), grown in the presence of an electric field at room temperature.
3. To investigate grown crystals with the help of different characterization techniques, such as (1) Powder X-ray diffraction (XRD) - To investigate the structure of produced crystals; (2) Thermogravimetric Analysis – To determine thermal stability and decomposition nature (3) Dielectric Analysis - To determine the type of polarization and the nature of electrical transport; (4) Impedance Spectroscopy - To determine the contribution of grains or grain boundaries in a. c electrical characteristics; (5) Modulus

Spectroscopy - To determine charge carrier transit and relaxation behaviour of crystals in an a. c electrical field; (6) Fourier Transform Infrared (FT-IR) Spectroscopy - For the determination of various functional groups and various normal modes of vibrations; (7) Ultraviolet-Visible (UV-Vis) Spectroscopy - To determine optical transparency, optical energy bandgap, refractive index dispersion and other optical parameters; (8) Photoluminescence - To determine luminous properties of emission and absorption, as well as the defect mechanism; (9) Relative Second-Harmonic Generation (SHG) efficiency - To determine the relative SHG efficiency of grown crystals.

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