Characterization of KH_2PO_4 Single Crystals added with L-Ascorbic Acid, DL-Malic Acid and Succinic Acid

by

POONGULAZHI.G

(20PPH013)

A dissertation submitted to the

Avinashilingam Institute for Home Science and Higher Education

for Women, Coimbatore-641 043

In partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

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CERTIFIED AS A BONAFIDE RESEARCH WORK

27/05/22

Signature of the

Head of the Department

27/2/2022

Signature of the

Supervisor

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INTRODUCTION

CHAPTER-I

INTRODUCTION

1.1 INTRODUCTION

The principle difference between the three states of matter, solids, liquids and gases is due to the separation and mobility of the atoms or molecules of which they are composed. In the gaseous state, molecules are highly mobile and separated by large distances. In the liquid state, molecules are in close proximity but still retain substantantial mobility. In the solid state, molecular motion is typically limited to vibration and intermolecular distances are at a minimum. Crystals are used in semiconductor physics, engineering, as electro-optic devices, so there is an increasing demand for crystals.

1.2 CRYSTALS

Solids may be either crystalline or amorphous in nature.A crystal is a regular array of molecular entities, ordered in 3D where this degree of order extends up to macroscopic dimensions. A single crystal is the one in which this 3D order extends up to the sample's physical size. Crystal in general, it is the 3D arrangement of atoms whose surface regularity reflects its internal symmetry as the solids are hard and firm. In polycrystalline solid, the crystal size is smaller than the actual sample size. Crystalline solids are characterized by long- range 3D order to exhibit a periodic three-dimensional pattern in terms of arrangement of component atoms of the solid. The structure of amorphous solids, closely resembles that of the liquid state where the short range is present and thermodynamically metastable. The repeating pattern causes the material to form all sorts of unique shaped and the process required is called crystallization [1].

1.3TYPES OF CRYSTALS

Solids are classified in terms of their degree and type of order. Three classes of crystals are **Crystalline solids, Semicrystalline solids & Non-crystalline solids.**

1.3.1 CRYSTALLINE SOLIDS

A solid is said to be a crystal if the atoms, molecules or ions are arranged in a three dimensional periodic manner or reticular structure. The regularity in appearance of crystals are viewed in nature and the crystals grown in laboratory. Therefore, the formed crystals convey that it is a regular repetition of identical blocks in 3D. Based on crystal shapes, when the crystal is subjected to constant environment, its geometry does not change and it will be a consequence of internal arrangement of constituent particles built up [1].

1.3.2 SEMICRYSTALLINE SOLIDS

It is also called as polycrystalline solids. A crystal is said to be a polycrystal if there are many crystallites contains in solid and grown together with interlocking mass, random orientation and separated by well-defined boundaries. The grains in the solid are not related in shape to crystal structure. The surface are in random shape and not well defined plates. The crystallites are randomly oriented, so the polycrystallites are isotropic. Examples of polycrystalline solids: Rock, Sand, Metals, Salts [1].

1.3.3 NON-CRYSTALLINE SOLIDS

It is also called as amorphous solids. These classes of solids do not have reticular or granular structure and it is the opposite extreme of the single crystal. The features of amorphous solids are they do not have definite melting point and due to the increase in temperature, the crystals become soft, viscosity drops and behaviour changes to ordinary viscous liquids. By observations, the crystallization takes place in amorphous solids due to the passage of time. Examples of Non-crystalline solids: Glass, plastic, resin, pitch, sugar candy. Applications of polycrystalline solids resulted after the certain passage of time are the crystals of sugar becomes sugar candy and the Glass “ ages” where the polycrystalline grains are formed, so the glass loses its transparency to become brittle [1].

1.4 PERIODICITY IN CRYSTALS

In order to distinguish the periodicity of the crystals, Bravais in 1848 introduced the concept of space lattice and translational vectors.

1.4.1 SPACE LATTICE &TRANSLATIONAL VECTORS

There are certain properties that distinguishes the crystals from other solids with the help of constituent particles such as atoms, ions or molecules which are arrangedin a three dimensional periodic pattern. Periodicity can be understood generally by the concept of space lattice and translational vectors. Translation (J) was carried out in an object to a finite distance (a) repeating systematically along the three crystallographic axes namely X, Y, Z axes for the purpose of obtaining three dimensional space lattice [1].

1.4.1.1 TRANSLATIONAL OPERATION

Translational operation repeats an object infinite number of times in one direction for obtaining one dimensional periodic array and J's are obtained. Nature of the repeated object does not affect translational periodicity. The periodicity is replaced by each object in array of points and the collection of points are called lattice. It is also called as one dimensional or linear lattice in certain cases. When a lattice point is imaginary, there will be a point which is an imaginary infinitesimal spot in space. Three dimensional arrays are obtained when the plane pattern has repeated in regular intervals, the first two non-coplanar translation combines with the third non-coplanar translation. The characteristic feature of the space lattice is the environment around any one point is identical with the environment around any other point on the lattice [1].

1.5 BASIS AND THE CRYSTAL STRUCTURE

Lattice point is an imaginary concept and necessary to distinguish a lattice from a crystal where the crystal structure is formed by associating every lattice point with an assembly of atoms or molecules or ions which are identical in composition, arrangement and orientation. When a 3 group of atoms or molecules are attached identically to each lattice point, a crystal structure is formed where the group of atoms or molecules is called basis. In general, basis is identical in composition and orientation and periodically repeated in space to form a crystal structure. The atomic arrangement in a crystal is called crystal structure.

Crystal Structure = Lattice + Basis.

Example: In copper and sodium, the basis is single atoms and in sodium chloride the basis is diatomic and in CaF_2 the basis is triatomic [1].

1.6 UNIT CELL

Smallest repeated unit with full crystal structure symmetry which is known as parallelepiped and six lattice parameters whose edges are a, b, c and the angles are α, β,γ were taken. Two non-collinear translations are explained on the basis of space lattice. Translation of a lattice is defined as line joining any two lattice points and in three dimensional which is considered to be simplest. Parallelepiped which is an infinite collection of such unit cells. The unit cell in general, is the smallest value repeated in all directions to build a crystal. The unit cell were selected by a primitive or a non-primitive cell. Primitive cell is defined by the parallelepiped with translations along the three crystallographic axes is minimum volume unit cell and with one lattice point whereas non-primitive cell contains more than one lattice points per unit cell. There is another way of choosing a primitive cell which is called as Wigner Seitz unit cell which was suggested by E.P. Wigner and F. Seitz. This cell is at a lattice point around the region of space closer to a particular point and conforms the translational symmetry to all lattice vectors. This cell leaves no empty space and there will be no overlapping and this method is same for both two and three dimensional lattices [1].

1.6.1 NUMBER OF LATTICE POINTS PER UNIT CELL

Number of lattice points in a unit cell depends on its nature and in a crystal structure, each point is occupied by a group of atoms or molecules. Lattice points are located only at the corners in a primitive cell. If the cell has eight corners, the number of lattice points per unit cell is one.In a crystal, there are body centered, base centered, face centered, rhombhohedral, primitive cell. In bcc, the lattice points are at eight corners at body centre which has two lattice points per unit cell. In fcc unit cell, the lattice points are eight corners and six face centers hence fourteen lattice points [1].

1.6.2 SYMMETRY ELEMENTS

Each arrangement of atoms as certain number of elements symmetry where rotation, translation, reflection and inversion comes under the symmetry elements. In crystallography, symmetry is used to characterize crystals, identify repeating parts of molecules. Repetition of an object by a translation leaves the environment around that object unchanged. Translation repeats an object infinite time while other operations repeat finite times.

There are various types of symmetry elements such as proper rotation, reflection, inversion centre, improper rotation, rotoreflection and rotoinversion. In proper rotation, when an axis said to have n-fold symmetry, it is represented by an angle ϕ passes through the centre or normal due to the reticular structure of crystals one to six fold rotational symmetry are possible. In reflection, it can occur in mirror plane or symmetry plane where the left handed object is transformed into right -handed and vice versa. In reflection, it can occur in mirror plane or symmetry plane where the left handed object is transformed into right-handed and vice versa. In inversion centre, it is called as centre of symmetry and operation is similar to reflection. The difference between reflection and inversion is reflection takes place in a plane of a mirror and inversion takes place in the centre of symmetry. In improper rotation, reflection and inversion takes place in enantiomorphous set of objects when rotational operation is also possible. In rotoreflection, rotation and reflection are combined to form a single hybrid operation. In rotoinversion, inversion is equivalent to reflection, possible to combine an inversion with an rotation to produce rotoinversion [1].

1.7BRAVAIS LATTICE

It is defined as three dimensional configuration of points which is used to describe the orderly arrangement in a crystal. This bravais lattice was discovered by the French scientist Auguste Bravais in 1850 with the help of fourteen types of unit cells for orderly arrangement of atoms found in crystals.

1.7.1 BRAVAIS LATTICE IN TWO DIMENSION

The bravais lattice takes place in two dimension or in a place lattice. Oblique lattice takes place where unlimited number of lattices will be possible as there is no restriction on length of lattice translations and the angles between them. The symmetry elements were restricted on the shape of the lattice and are called as special lattices. The lattice types are oblique, square, hexagonal, primitive rectangular and central rectangular with a conventional unit cell such as parallelogram, square, rectangle, 60^0 rhombus etc., axes and angles with point group symmetry about lattice point [1].

1.7.2 BRAVAIS LATTICE IN THREE DIMENSION

The bravais lattice takes place in three dimension or in a space lattice. There was a restriction in lattice translation and angles in two dimensions whereas in three dimensions similar restrictions were applied by which there are restrictions takes place in the lattice translations and the angles with only fourteen types of lattices and generally triclinic and thirteen special crystal lattices are applied. This restrictions are collectively called as Bravais lattice in order to specify the given arrangement of points in a space lattice or atoms in a crystal. The fourteen lattices are divided into seven crystal systems and they are triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic. The crystal with no restriction and the angles are equal is called as triclinic system. There will be a two fold symmetry with two axes perpendicular parallelepiped in one direction is called as monoclinic system. Two fold symmetry with three mutually perpendicular directions are called as orthorhombic systems. The cubic system is taken as the highest among all symmetry where three crystallographic axes are orthogonal and equivalent with three lattices which are simple cubic, body centered cubic and face centered cubic lattice [1].

1.8 MILLER INDICES

The Miller indices are defined as the group of three numbers which indicates the orientation of a plane or set of parallel planes of atoms in a crystal. The first lattice plane hx+ky+lz=1 nearest to the origin will be a set of parallel, identical and equally spaced planes. The resulting set of three integers h, k, l are enclosed to parentheses (hkl) are called Miller indices which is used to describe the lattice plane. The Miller indices can be obtained by determining the intercepts x,y,z in lattice parameters and divide their intercept ts and confirm that there is no reciprocal. When the result is in fraction, multiply by a common divisor and put in the h k l and the miller indices are obtained. The Miller indices are represented when three crystallographic axes are known by taking the reciprocals of the given Miller indices where the intercepts are taken of axial units to mark the length of the intercepts on coordinate axes to join the end points [1].

The interplanar spacing {h k l} for lattice planes with Miller indices d (h k l) in a crystal lattice equal to the reciprocal of the norm of n perpendicular to the (h k l) lattice planes. In general, it is the perpendicular distance between two successive planes in a family (h k l) which is commonly indicated asd_{hkl} .Indexing crystal planes and direction are possible for deriving formula for spacing between two consecutive parallel planes in a given unit cell and are expressed in an orthogonal coordinate axes to obtain simple Cartesian geometry. Three mutually perpendicular axes and plane are parallel which is passing through the origin to make intercepts on three axes. Interplanar spacing of various crystal systems are cubic, tetragonal, orthorhombic, hexagonal, rhombohedral, monoclinic and triclinic [1].

1.9 CRYSTAL GROWTH METHODS

Super saturation is the basic condition to be attained to grow a crystal with the process of nucleation. To grow a crystal, there are some basic condition for crystallization process which are called as supersaturation and also slow cooling process. There are various properties which differ in the growth of the crystal such as physical and chemical properties, solubility, melting point, decomposition, phase changes. The crystal growth depends upon the characterization of materials which we are investigating such as its melting point, volatile nature, solubility in water or other organic solvents.

1.9.1 GROWTH FROM MELT:

This growth process comes under crystallization which is generally based on freezing. The rate or growth is normally much higher than other methods. In this method there were no impurities added in this growth process which is the important method for crystal process. Further this method is classified into sub-groups or various techniques.

- Bridgemann method
- Czochralski method
- Vernuil method
- Zone melting method
- Kyropoulos method
- Skull melting.

The Bridgemann method is a method of growing single crystal ingots or boules which involves heating a polycrystalline material. The Czochralski method is used for growing semi conducting material crystal. The Vernuil method is used for chemically pure fine powder and also used in oxygen hydrogen flame for lowering mechanism. The zone melting method involves a liquid zone which is created by melting method or long solid charge. The Kyropoulos method are used for cooled seed to initiate single crystal growth and skull meting involves growth of high melting point materials [2].

1.9.2 VAPOUR GROWTH

This method is very mainly used to grow bulk crystal with the aid of crystallization process and also used in epitaxial films and thin coatings. They were also divided into two sub groups which is called as 1) Chemical Transport method 2) Physical Transport method.

In chemical transport method, the material is transported as a chemical compound and in physical transport, evaporation or sublimation takes place. Example: Crystals of silicon, diamond, gas, semiconductor compounds [2].

1.9.3 SOLUTION GROWTH

This method is also used for obtaining bulk crystals where the crystals are grown from aqueous solution. There are four types of solution growth methods and they are

a) Low temperature solution growth
b) High temperature solution growth
c) Hydro Thermal growth
d) Gel growth.

a) In **low temperature solution growth** method, there are various solvents used such as water, ethyl alcohol, acetone. It is also called as slow cooling method, slow evaporation method, temperature gradient method. The slow cooling method is the process in which the saturated solution are poured in a crystallizer and is thermally sealed. After the seed crystal is suspended, and the crystalliser is kept in the water with a thermostat, the solution remains in the solution at the end of the run.

In **solventevaporation method,** it is contrast to the cooling method and there will be an excess of given solute with the difference between the rates of evaporation of the solvent and the solute.

In **temperature gradient method**, the transport of the material is from hot region and in the cooler region, they form super saturated solution.

b) In **high temperature solution growth** method, the solvents are generally effective also the low temperature solution growth are also employed. The process takes place when the solution attains supersaturation in crystallization process which are dissolved in a suitable solvent. Flux growth is the very important and the widely used high temperature solution growth method.

c) In **hydro thermal growth method**, growth from vapour and solutions plays an intermediate case and the liquids involved in this process are usually alkaline aqueous solutions and the growth is carried out in steel auto claves or silver linings. The materials which are grown by this hydro thermal growth method are calcite, alumina, antimony. Single crystals grown by this method are diamond, barium titanates. This process does not favour for the crystal of high temperature.

d) In **gel growth method**, there are certain principles used here. It is nothing but the crystallizations takes place when solution of two suitable compounds give rise to crystalline substance by more chemical reactions. It is also one of the main growth method when compared to the other methods.

X (in solution) + Gel medium on atm pressure gives X (crystal).

There are various types of gels in crystals which is called as physical or chemical gels.The gel which is obtained by physical process such as cooling is called physical gels. Gelatin, clay comes under this type of physical gel. The gel which are obtained by chemical reactions such as hydrolysis or polymerization are called chemical gels. Silica, polyacryalamide comes under this type of chemical gels [2].

1.10 APPLICATIONS OF CRYSTALS

- Molecular crystals has wide application in pharmaceuticals, pigments, explosives, metal-organic frameworks [3].
- The most practical usage of crystallization is salt crystallization as it is the most cost effective way to produce salt even at today [4].
- Crystal also has wide application in compound purification and crystal production [4].
- Silicon single crystal and quartz are the most significant materials for the semiconductor industry [5].
- Optical crystals, high temperature superconductors, scintillators for medical imaging, piezo electric crystal, magnetic crystals and topological insulators can be done by hydrothermal method [5].
- Single crystal scintillators and germanium semiconductor detectors are used in oil well logging tools for gamma ray radiation [6].
- The only semiconductor used in current is high purity germanium [6].

1.11 OBJECTIVES

The objectives of the present work are:

1. To grow pure KDP single crystals.
2. To add Succinic Acid, L-Ascorbic Acid and DL-Malic Acid to KDP.
3. To harvest and study the characteristics of the grown crystals using Powder X-ray Diffraction, Fourier Transform Infrared Spectroscopy, Ultra Violet- Visible, Thermal Studies and Non-linear optical studies.

REVIEWS OF LITERATURE

CHAPTER 2

REVIEWS OF LITERATURE

2.1 INTRODUCTION

Nonlinear optical materials have evolved slowly over the past 20 years. If the intensity of illumination gets high enough, nonlinear optical effects can occur and the optical properties become intensity dependent. The nonlinear optical material must be highly transmitting at the fundamental and harmonic wavelengths and must have a laser-induced-damage threshold high enough to allow optical intensities that will provide adequate conversion efficiency. Phase matching must be possible in the material.BBO (β-barium borate), KDP (potassium dihydrogen phosphate), KTP (potassium titanyl phosphate), lithium niobate, polymers and copolymers are some of the examples of NLO materials.They can be applied in many optical devices, such as thin film and fiber waveguides. In particular, polymeric thin films that exhibit large second- or third-order optical nonlinearities have many useful applications in integrated optics, such as optical modulation, optical switching and optical data processing. In this chapter, the journal articles pertaining to NLO material KDP and KDP doped crystals are analyzed.

2.2 REVIEWS ON SHG MATERIALS

K.Manimekalai and P.Jayaprakash, (2021) have grown the NLO crystals of KDP and KCL by slow evaporation technique. The reflected lines of doped KDP was correlated well with pure KDP by slight shift in intensity of diffracted peaks by Powder X-ray diffraction (PXRD). The tetragonal system and IG2d space group was determined by single X- ray diffraction (XRD). The functional group of harvested crystals were confirmed by Fourier Transform Infrared Spectroscopy (FTIR). Crystals having transmission in visible range were confirmed by ultra Violet- Visible Near Infrared Radiation (UV-Vis NIR). Green light emission of KDP and Potassium Chloride doped KDP (PCKDP) was confirmed by Second- Harmonic Generation (SHG) and the soft material category was confirmed by Victor-Mayer test [7].

M.Esthaku Peter et al., (2021) have grown succinic acid doped with KDP crystal by a slow solvent evaporation technique. Compound confirmation was done by X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR) analysis. The wide transmittance ranged from ultraviolet to infrared region. The doped crystal was made to find application in deep ultraviolet non-linear optical device by Ultra Violet-Visible Near Infrared Radiation (UV-Vis NIR) spectrum. Second- Harmonic Generation (SHG) of succinic acid doped KDP was 1.25 times greater than standard KDP. By Vicker'smicrohardness test, the mechanical hardness was greater than other doped KDP crystals higher thermal, mechanical stability and Second- Harmonic Generation (SHG) efficient were possessed by these crystals and could be utilized in laser and photonic device fabrication [8].

DhanpalBairawa et al., (2021) have grown large crystals of Potassium L-Ascorbate monohydrate by solution growth technique by lowering at the rate of 0.24^0C/ h and the water was used as a solvent. By single- crystal X-ray diffraction (XRD), the structure of Potassium L-Ascorbate monohydrate (KLAM) were crystallised in monoclinic P_2, space group and the bulk morphology was possessed by the crystals. Potassium L-Ascorbate monohydrate (KLAM) was thermally stable upto 80^0C by TGA/ DTA. The good optical transparency was offered by the crystal with lower cut off as low as 297 nm. Powder sample was 3.5 times that of KDP was measured by Second- Harmonic Generation (SHG).On the α-plate of Potassium L-Ascorbate monohydrate (KLAM) , the phase matching (PM) was observed. Non collinear phase matching rings were observed near PM directions and helped to identify PM directions. The observation of non collinear second harmonics ringed upto third order indicated high magnitudes of non linear optical coefficients. Single pulse laser threshold value of the crystal was 3.074 GW/cm^2 at 1064 nm on α-plate of the crystal [9].

S.P. Ramtekeet al., (2020) have investigated the growth and optimization of optical traits of copper sulphate crystal exploiting L-Ascorbic acid for photonic device applications by slow evaporation process. The triclinic crystal planes and structural parameters were identified by Powder X- ray Diffraction (PXRD), the Fourier Transform Infrared Spectroscopy (FTIR) confirmed C=O group with carboxylic group of L-ascorbic acid and copper sulphate, the optical transmittance was about 76% and 87% in L-ascorbic acid and copper sulphate,irradiation of He-Ne conveyed that -nonlinear refraction of Copper Sulphate (CuS) crystal was positive while the influence of L-Ascorbic acid altered it to negative. They studied that L-Ascorbic acid was a potential optimizer of optical traits and used for industrial photonic devices [10].

D.Kanimozhi et al., (2019) have grown KDP by slow evaporation method and three dyes alizarine, cango red, evans blue were doped. The cell parameters were found by Powder X-ray diffraction (PXRD), optical behaviours were studied by Ultra Violet Visible absorption spectrum, functional group analysis by Fourier Transform Infrared spectroscopy (FTIR), emission characteristics using photoluminiscence study of pure and doped KDP were studied. They have also showed the better frequency conversion property of crystals by Second Harmonic Generation (SHG) and grown crystals were studied by laser damage threshold study in pure and doped KDP. By etching analysis, growth pattern were examined, mechanical stability was determined by Vicker's micro hardness study and for different frequencies dielectric studies were also carried out in pure and doped KDP [11].

A. Venkatesan et al., (2018)have grown Non-Linear Optical (NLO) single crystals for opto-electronic applications with L-Malic acid doped KDP by slow evaporation method. Tetragonal structure was confirmed by XRD and the functional groups was determined byFTIR. Wide optical window, no absorbance, good transmittance in the entire visible region was confirmed by Ultra Violet- Visible (UV-Vis) spectra.Second Harmonic Generation (SHG) confirmed the NLO studies that was 1.4 times greater than reference KDP.The electrical property of the grown crystal was observed by the dielectric studies.Thermo Gravimetric Analysis(TGA) and Differential Thermal Analysis (DTA)thermogram revealed the thermal stability of the materials. Photoluminescence studies showed the excitation of L-Malic acid doped KDP (LMKDP) falled in violet and red fluorescence spectrum [12].

BotondSzilágyi, et al., (2018) have done experimental implementation of a quality-by-control (QbC) framework using a mechanistic PBM-based nonlinear model predictive control involving chord length distribution measurement for the batch cooling crystallization of L-Ascorbic acid. Two states of -art Quality-by-Control were the direct nucleation control (DNC) where there was a feedback control despite an oscillatory control and a novel nonlinear model predicative control (NMPC) framework to reduce the batch time and overcome the process nonlinearity and apparent time delay. Using chord length distribution (CLD) data, they has detected the kinetic parameters and NMPC proved to be highly robust even under large plant model mismatch and sensor and/or communication failure [13].

Yoko Tominaga et al., (2018) have prepared and the sustained release of titanium dioxide hollow particles encapsulated L-Ascorbic acid. They have done through sol gel processing using inkjet nozzle and the morphology of titanium dioxide particles were evaluated by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectrometry (EDS). They estimated the sustained release in titanium dioxide by dialysis bag method in phosphate buffer saline and exhibited special porous structures, in addition they found that the degradation of L-Ascorbic acid was inhibited by encapsulated Titanium dioxide and L-Ascorbic acid [14].

S.Arulmani et al., (2018) have studied the thermal and dielectric properties of L-Malic acid doped KDP single crystals as that was used for frequency conversion process by slow evaporation method. They added L-Malic acid of 0.2 molar % of KDP and there was homogenization. PXRD conveyed that the crystal belong to tetragonal structure at the range of 10- 70^0. In FTIR, an intense band of strong absorption around 1217 cm^{-1} and carbonyl group gave hydrogen bonding and O-H stretching vibration also explained the confirmative group of the water on hydration. By SHG analysis, they used KDP as the reference material and founded that L-Malic acid doped KDP (LMKDP) was 1.4 greater than reference KDP. By dielectric studies, they have studied the frequency at range of 50 Hz to 50 MHz. The high value of dielectric constant resulted in the presence of four polarizations that are space charge, orientation, electronic and ionic. By optical absorption studies, the UV-Vis spectrum of L-Malic acid doped KDP (LMKDP) crystals were recorded and used for the investigation of NLO and spectroscopic absorbance. These properties of crystals were used for device fabrication. By thermal stability,TGA and DTA were studied simultaneously. TGA showed that L-Malic acid doped KDP (LMKDP) was stable upto199^0C and DTA showed that good crystalline nature of the title compound was exhibited. Photoluminescence studies conveyed that intensity majorly depends on excitation energy and intensity of the incident beam [15].

K.Manimekalai, R.Rajasekaran (2017), have worked on succinic acid added in the ratio 1:1 molar percentage to KDP and has grown single crystal by slow evaporation method. Single XRD revealed that crystals were tetragonal and belong to I42d space group. PXRD determined the incorporation of succinic acid into KDP crystal lattice. FTIR confirmed the functional group of dopant present in the grown crystal. Transmission observed in visible range was confirmed by UV-Vis. Kurtz Perry Powder method was used to test the efficiency of relative SHG and revealed the moderate NLO property on the grown crystal. Dielectric constant and dielectric loss were decreased with increased frequency. Hardness studies confirmed that it was a soft material and a good material for photonic device fabrication [16].

R.Raja et al., (2017) have grown KDP dopedAdipic acid crystals by slow evaporation technique, the presence for functional group for the compound and the dopant was confirmed by FTIR. The absorption and transmission of the crystal was observed by UV-VIS spectrum. The thermal stability of the crystal from the TG curve, in the crystal was confirmed by the thermal analysis, there was no weight loss up to 220 ºC. The crystal was thermally stable for device application. SHG confirmed by the emission of green radiation which was a potential material for frequency conversion. The Vickers microhardness test was carried out for the grown crystal the result revealed the mechanical properties of the grown crystal. Material belonged to hard material category was confirmed by Mayer's index number (n) [17].

Mohd. Shkir et al., (2017) have studied the remarkable effect of L-Ascorbic acid on crystal morphology, structural, crystalline perfection, optical and photoluminescence, dielectric properties of zinc (tris) thiourea sulphate (ZTS) single crystals by slow evaporation technique. By structural analysis, extra phase has been identified due to the presence of L-Ascorbic acid, crystalline perfection was confirmed by High-resolution X-ray diffraction(HRXRD), low optical absorbance and high band gap resulted in optoelectronic devices. Dielectric constant was improved due to the presence of dye. In characterization method, the Powder X-ray diffraction (PXRD) was done with CuKαradiation and the optical properties were studied in solid as well as in solution using UV-Vis-NIR spectroscopy. Photoluminescence emission spectra were observed by Lumina Fluorescence spectrometer and there was an enrichment of crystallinity. Single phase was confirmed by X-ray diffraction (XRD) and by UV-Vis-NIR, energy gap studies grown crystals were having very low absorbance and high optical transparency. By photoluminescence analysis, the emission spectra were measured at three different excitation wavelengths such as 310, 358, 385 nm for all the crystals. Dielectric studies confirmed that it was applied mainly in solid state devices and explained about electro-optics. The capacitance(C), tan δ, impedance (Z) were also measured in frequency range from 3KHz to 10MHz [18].

Krishna Kumar et al., (2016) have studied the simple 2D composite image analysis technique for the crystal growth of L-ascorbic acid.Growth experiments on the L-ascorbic acid crystals were carried out by standard (optical) microscopy, laser diffraction analysis, and composite image analysis. By image analysis, the growth was captured as digital 2D RGB images and the crystal boundaries emerged as white lines not as black background and they were well differentiated by peaks in intensity graphs where the graph measures length of the crystal boundaries. The length measured by laser diffraction were correlated with both the techniques for growth of L-Ascorbic acid [19].

MohdAnis et al., (2015) have grown KDP and Formic acid (FA) of dimension $21\times15\times9$ mm^3 by slow evaporation method. They have characterized this crystals using XRD and confirmed the cell parameters, incorporated FA in KDP by Fourier Transform Infrared Spectroscopy (FTIR), recorded the range of 200 to 900 nm using Ultra Violet Visible (UV-Vis) absorption spectrum and in the visible region, colour centred photoluminescence emission spectrum has been illustrated. FA doped KDP by Vicker's micro hardness test hardness parameters were calculated. Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were used to examine the thermal stability effect of FA on KDP. Dielectric behaviour were also studied [20].

MohdAnis et al., (2015) have investigated the non-linear optical property on oxalic acid (OA) with maleic acid (MA) grown by slow evaporation technique and characterized the dielectric behaviour of potassium dihydrogen phosphate by SHG analysis, Z-scan and dielectric studies. SHG efficiency was confirmed by Kurtz Perry Powder test, the close and open aperture Z-scan technique have been employed to study the nature and origin of improved third orderNLO behaviour of doped KDP crystals at 632.8 nm. Using Z-scan transmittance, magnitude of third order nonlinear susceptibility, nonlinear refraction, nonlinear absorption coefficient and figure of merit (FOM) of doped KDP crystals were calculated. The dielectric constant and dielectric loss of pure, OA and MA doped KDP crystals were measured at different temperatures by means of dielectric studies [21].

PratyaThongpanit et al., (2013) have grown single crystal of boric acid doped KDP by evaporation method. PXRD confirmed the crystal structure of grown crystal and FTIRanalysis confirmed the presence of all functional groups. The thermal study by TGA revealed the different stages of decomposition. The thermal stability of the doped crystals was found to be improved due to presence of boric acid. The microhardnessvalues of doped KDP crystals were found to be increased by the presence of dopant boric acid. This result indicated that the grown crystals are useful for device application [22].

HoudaEttoumi et al., (2013) have characterized the properties of KDP doped with Cu^{2+} and PXRD revealed that KDP does not change the structure when added to Cu^{2+}. By DTA and Raman spectroscopy, two phase transitions took place (Ttr = 453 and 473 K). Measurement of polycrystalline pellet of Cu-KDP temperature was 495 K by electrical conductivity and only one phase transition took place at 470 K. The activation energy was 0.42 eV from RT to 470K. Above 470K, 1.87 was the activation energy of supertonic phase [23].

P.Rajesh et al., (2013) have grown crystal violet dye doped potassium dihydrogen phosphate single crystal by Sankaranarayanan- Ramasamy method and slow cooling method with the vision to improve the properties of the crystal and showed how organic dyes influenced the growth, morphology of potassium dihydrogen phosphate crystal. The grown crystals were of size up to 130 mm in length and 10 mm in diameter. The incorporation of dye was more in the crystal grown by slow evaporation method compared to the crystal grown by Sankaranarayanan- Ramasamy method. The addition of dye improved the quality and yields more than 90 % transparent crystals and also growth rate was very high. Thermal stability of the doped crystal was high compared to pure crystal. Low dielectric loss shows that the grown crystal contains minimum defects. The optical transmission, thermal and mechanical stability showed the suitability of the ingot for optical applications [24].

BoguszawaWierzbowska et al., (2011) have done continuous mass crystallization of Vitamin C in L(+)-Ascorbic Acid ,ethanol ,water systemwith the size-independent growth kinetic model approach. Constant feed concentration of ethanol (20 mass %), the feed concentration of vitamin C was changed within the 30-50 mass % range and the mean residence time of suspension varies from 900-3600 s and resulted in a productivity2441692 kg/(m^{3}h) of crystal product, size was about 0.200.24 mm and of CV within the 5060% range. The super saturation level was reached in mother solution with a short mean of residence [25].

K.Srinivasan and K.Vanitha Devi (2010) havegrown single crystals of L-Ascorbic acid popularly known as Vitamin-C by low temperature solution growth method. They were grown with different solvents and solvent combinations such as acetone, ethanol, methanol, isopropyl alcohol, water, water+ acetone (1: 1), water + ethanol (3:1) and ispropyl alcohol + methanol (1:1) was found by solubilty and crystallization behaviours. By Gravimetric method, the solubility of L-Ascorbic acid in selected solvents and solvent combinations in a range of temperature was determined. Solution prepared with water, water + acetone (1:1), water + ethanol (3: 1) and water + isopropyl alcohol (3: 1) were yielded crystals and their morphologies were evaluated by Goniometry. The monoclinic system with point group 2 and space group P_2 and lattice parameters determined in line was confirmed by PXRD. Functional groups in crystal compounds were characterized by FTIR. Optical transparency was observed between 330nm to 1400 nm and materials doesnot have any phase transition and was stable upto that melting point was confirmed by DSC. NLO characteristics were confirmed by SHG and wavelength in Infrared (IR) region when exposed to high power laser source [26].

P.Rajesh et al., (2010)have studied properties of ADP with the help of DL-Malic acid and Cobalt (II) acetate hexahydrate. Good transparency for non linear optics was confirmed by UV-Vis. By Vicker's hardness test, the crystals face was (1 0 0) and the hardness was increased with the dopant of DL-Malic acid. Dielectric studies revealed the dielectric constant and dielectic loss for different frequencies and temperature. DL-Malic acid and ADP showed low dielectric loss and the crystalline perfection was confirmed by HRXRD. Good piezoelectric behaviour were also studied and SHG studies confirmed that DL-Malic acid doped was greater than pure and cobalt (II) hexahydrate [27].

Qiangguo Wang et al., (2009) haveinvestigated rotary ultrasonic machining of KDP on surface roughness where KDP was used as electro-optic parts, hard to machine material, soft, brittle and anisotropic properties. They have investigated about the influence of three process variables (spindle speed, ultrasonic powder, federate) tool design on surface roughness in RUM of KDP. In the range of 2000–6000 rpm, a higher spindle speed produced higher roughness (rougher surfaces). Within the tested range (from 20% to 40%), ultrasonic power was not a critical factor in determining the roughness. Surfaces became rougher as the federate increased. Depending on the federate value used, RUM could produce either smoother or rougher surfaces than diamond drilling. Surfaces obtained when using a tool with a chamfered corner were smoother than those obtained using tools with right angle corners. Smaller diamond grains tended to produce smoother surfaces the effects were less significant than the tool design (tools with a chamfered corner versus a right-angle corner [28].

D.Jaikumar et al., (2009) have grown L-alanine doped with DL-Malic acid by slow cooling technique in the ratio 2:1 for synthesis of size $24\times13\times8mm^3$ by 26 days. Orthorhombic system was confirmed by XRD and crystalline perfection was studied by HR-XRD. The vibrational frequencies of various functional groups were studied by FTIR. By TGA analyses, the sample was found to be thermally highly stable (224^0C). The frequency doubling of the grown crystal and their efficiency was nearly equal to KDP was confirmed by SHG Kurtz powder test. These crystals could be used as promising materials for NLO applications and used for fabrication of electro-optic devices. Young’s modulus of the grown crystal was calculated as 0.7018×10^{10} N/m^2 was confirmed by Knoop Hardness test [29].

P. Rajesh, P.Ramasamy (2009) have grown single crystals of DL-malic acid doped ADP and properties of ADP was improved by Sankaranarayanan-Ramasamy (SR) method. PXRD analysis indicated that the structure of crystals remains same after the addition of 1 mol % DL-Malic acid. The shift in FTIR was proved by the presence of DL-Malic acid in ADP crystal. The transmission spectrum of the crystal revealed that the grown crystal had sufficient transparency in the entire visible region and transparency was higher in SR method than conventional method. Hardness value was increased in DLM- doped crystal by SR method than by conventional method. Good crystalline perfection was confirmed by HRXRD analysis. ADP crystals generated optical second harmonic frequency of an Nd: YAG laser and it was 1.5 times higher than pure ADP.High-quality, large-size ADP crystals with faster growth rate were grown by the addition of 1 mol % DL malic acid in ADP [30].

M. Meena and C.K. Mahadevan, (2008) investigated KDP and ADP with L-Arginine grown under solution methods where DC and AC electrical measurements were carried out and resulted in increase of electrical parameters with increase of temperature and lead to L-defects. They have also determined the electrical conductivity of the KDP group crystals by proton transport within the framework of hydrogen bonds. They also found that the addition of L-arginine lead to decrease of electrical parameters in both KDP and ADP with low ε_r value dielectrics [31].

Xieu Ren et al., (2008) have investigated the fundamental growth behaviours of KDP, ADP and mixed KADP. They have also determined the solubility curves of KDP and ADP crystals measured by traditional weight analysis. Conventional methods such as composition dependent experiment by slow evaporation technique and time dependent experiment were also used in the growth of KDP hybrid crystals. They also concluded by comparing the solubility of KDP and ADP and found that molar concentration of ADP was two times that of KDP.The growth along the a-axis was mainly controlled by the constituent H_2PO_4 $-$anions that was sensitive to the growth conditions and the stronger bond strength of K-O bond, the growth rate along the c-axis of KDP was faster than that of ADP. For KADP crystals, the competitive growth between $NH_4^+$and K^+ ions wasan important factor, which lead to the reduction of the growth rate along the a-axis [32].

S.S. Hussaini et al., (2007) have grown KDP crystals with thiourea by low temperature solution growth method. By PXRD, they confirmed its crystal structure. In FTIR, the frequency was slightly shifted and UV visible spectra has shown this crystal was applicable for opto electronics than pure KDP. SHG enhanced the non-centro symmetric structure of host and there was an increase in non-linearity. TGA showed that crystal was thermally stable upto230^0 [33].

S.Krishnan et al., (2007) havegrown single crystals of succinic acid by slow evaporation method and monoclinic system with space group P21/C was confirmed by XRD. Transparency of crystals were confirmed by UV absorption spectrum. Molecular vibration and functional groups was confirmed by FTIR. Thermal stability upto240^0 was confirmed by TGA/ DTA. Very low dielectric constant values, pyroelectric properties and low dielectric loss revealed the crystals purity were confirmed by dielectric studies [34].

Dongli Xu, DongfengXue, (2006) have employed Bond Valence Method (BVM) and calculated bond strength in which the chemical bonds were formed between KDP and ADP. They have also calculated and compared the relative growth rates of all selected plane, related to crystal structure and chemical bond strength. The natural morphology of KDP from crystallographic structure and chemical bond strength was deduced. Theoretically, they found the bond valence by considering all the atoms as cations and anions and determined the atomic positions on the basis of BVM. Ethanol, as an anti-solvent on crystal morphology was microscopically interpreted [35].

S.Goma et al., (2006) have grown KDP single crystals added with urea by the slow evaporation method from aqueous solutions. Dielectric measurements were carried out along both the unique axis and perpendicular directions at various temperatures ranging from 313 to 423 K by the conventional parallel plate capacitor method. The study shows that the dielectric parameters increase with the increase in temperature but do not vary systematically with respect to impurity concentration. Also, it indicates that 0.6 mole% urea addition to KDP leads to low permittivity value dielectrics [36].

Kunpeng Wang et al., (2006) have studied the laser-induced damage mechanisms and improvement of optical qualities of bulk potassium dihydrogen phosphate crystals. They founded that the low damage threshold of KDP greatly limits the application in all fieldsand reviewed the studies of laser-induced damage mechanisms and optical qualities of KDP in recent years. Multipole ionization, collision ionization, heating, stabilization mechanisms of electron–hole compound point defects were the laser induced damage mechanisms and crystal growth process, post treatment methods were the optical methods in KDP improved by them [37].

Guohui Li et al., (2004)have investigated a chelating reagent sulfosalicylic acid (SSA) as a new additive was added into the KDP solutions in a small amount (1 wt%) and metastable zone widths were measured for different saturation temperatures when compared to the pure system. Potassium dihydrogen orthophosphate crystals (KDP) were rapidly grown from both pure and SSA-added solutions by adopting the same crystal growth procedure. The crystal grown from SSA-added solution was subjected to optical transmission and laser damage threshold studies as compared with the crystal grown by traditional growing method [38].

Miho Ito et al., (2003) have investigated the morphological diversity in crystal growth of L-Ascorbic acid dissolved in methanol. They have presented morphological diagram in crystal growth of L-ascorbic acid called vitamin C from methanol solution on a flat glass dish and observed three kinds of patterns such as homogeneous disk, concentric ring and dendrite in the growth of L-Ascorbic acid by varying the humidity and initial concentration in methanol solution. The crystals could be grown in any patterns were observed in higher concentrations less than 90% humidity and cross overs were also observed from one pattern to another [39].

N.Zaitseva et al., (2002) have grown KDP and DKDP crystals at the rate of 10-20 nm/ day and the linear size was 90 cm. They have employed various growth techniques that were 1) Creation of special dislocation structures during seed regeneration process 2) Change in orientation of the seed to control the ratio of dimensions along the crystallographic axes. The normal growth rate was determined with the help of steepinessand the tangential growth rate of dislocation step. By rapid growth technique on a point seed, crystals of various sizes were grown with real and equal concentrations were found. With dislocation control during seed regeneration, they have grown strong dislocation bunches on the faces of crystals by 4 techniques and found the pyramidal faces under the crystallographic axes. In habit variations by the change of seed orientation crystals had grown faster in X-Y than Z-direction of {100} direction by the difference in deutration level between seed and crystal. They have concluded that with the help of these crystals rectangular cross section resulted due to limitation of growth of one prismatic face by the platform [40].

J.Podder (2002) have grown KDP crystals with urea and KCL in different molar ratio by slow cooling method. Effect of impurities on growth, nucleation kinetics, surface morphology, structural, optical mechanical properties were investigated by them. Higher mechanical stability in urea doped KDP was higher than KCL was confirmed by Vicker'sMicrohardness test. The optical quality was better in urea doped KDP than KCL doped crystals. The green signals emitted by the urea and KCL doped KDP crystals was confirmed by SHG [41].

H. Uesaka, R. Kobayashi (2002) have studied the pattern formation in the crystallization of ascorbic acid when it was crystallized from methanol solution. Formation of concentric rings causedby the oscillatory crystallization was done to identify the pattern formation in Ascorbic acid with the mechanism of void-fluid interaction as that was responsible for oscillation and formation of periodic structure. They have examined that similar concentric rings were found in the materials with needle crystal form for fluidization process and bacterial colonies were also formed as the result of pattern formation [42].

J. J. De Yoreoet al., (2002) have developed KH_2PO_4(KDP) and KD_2PO_4(DKDP) crystals for the world's most powerful laser. The NIF was housed with 122 by 170m building with U shaped configuration and Optical homogeneity was achieved for larger crystals with higher consistency. KDP crystals were grown on two sets of faces {101} pyramidal faces and {100} prismatic faces, where supersaturation was exhibited in all the experiments and processed by (AFM) atomic force microscopy. It was shown that {101} face is K+ terminated and {100} face was terminated by altering the rows in K+ and $H_2\,PO_4$- ions. They have used Continuous filtration system to grow the crystals covered with dislocations and resulted in regeneration from seed with optical homogeneity and laser damage threshold. Relative growth rates of various prism were determined by crystal habits and high dislocation density have resulted in large degree of optical distortion. They also has studied that before NIF system, surface damage threshold of diamond turned KDP and DKDP crystals were significantly higher than bulk damage threshold for diamond turned surfaces [43].

Elly van der Voort (1991) havegrown succinic acid crystals from aqueous solution were platy with (1 0 0) basal plane and side faces (1 1 1) and (0 1 1) where the crystals grown from iso-propanol were needle-like (1 0 0) (0 1 0) plates. PBC analyses were not predicted by these habits. In screw dislocation mechanism, the role of solvent was related to habit controlling factors. With the aid of molecular mechanics calculations, the solvent interactions with various faces of succinic acid crystals was determined. In a semi- quantitative way, the habits from water and from iso-propanol were explained [44].

Takatomo Sasaki and Atsushi Yokotani, (1990) have grown KDP crystals of 40cm × 40cm cross section used as frequency converted of high power laser system for nuclear fusion experiments. Using Temperature Reduction Methods (TRM), the crystals were grown at a rate of 1-1.5mm/ day and by using Three Vessel Method (TVM) the crystals were grown at a rate of 2.9mm/day and constant super saturation techniques were also employed. The bulk laser damage threshold was improved by reducing organic impurities in growth solution [45].

A.Yokotani et al., (1986) have grown crystals under irradiation of UV radiation and found that the growth of microbes were reduced in KDP by UV radiation than usual methods. They also studied the microbes in KDP by using water sampler from Millipore Limited where gel-like samples appeared on the sample and Q-switched $\mathrm{Nd^{3+}}$:$\mathrm{LiYF_4}$ (YLF) laser were also used to measure bulk damage threshold and He-Ne laser located the small damage spots [46].

H. Newkirk et al., (1983) havecharacterized KDP crystals by X-ray topography and the volumes in KDP crystals were damaged by 1ns, 1064 nm laser pulses. Non uniform distribution of defects, linear dislocation networks, cracks, transition or growth layers, sectors and inclusions were exhibited by these crystals. They have also detected the damaged volumes by spherically symmetric radial strain field and found there was an unambigious correlation between the pre-existing X-ray topography microstructure of a test volume and its laser damage threshold. In some crystals, threshold were least in test volumes and in other crystal, volume of free defects had least thresholds. Some entity was not resolvable by X-ray topography and a point defect impurity cluster was the limiting cause of damage [47].

R.J.Danvey et al., (1981) have grown succinic acid from aqueous solution that were plate like dominant (001) basal plane from isopropanol solution and grown needle-like crystals. Succinic acid structure played by solvent was not predicted by periodic bond chain analyses. Relevant solution chemistry and measurement of crystal growth kinetics in two solvents were observed morphological change in terms of solute-solvent interactions [48].

Y.M. Fishman (1977) have studied the defect structures of DKDP grown on seed crystals cut from KDP by X-ray diffraction topography. Plate (011), top pyramid (011) and plate (001) were three types of seed grown by them. In (011) elastic stresses were observed due to difference in lattice parameter. The plane (011) in DKDP was misoriented by an angle of several minutes and in top pyramid seeds except misorientation was varied both from one growth sector to other and in perfection of DKDP on KDP (001) was rather high [49].

MATERIALS AND METHODOLOGY

CHAPTER-3

MATERIALS AND METHODOLOGY

3.1 INTRODUCTION

The crystal is characterised for the purpose of knowing the chemical composition, the crystal structure, the defects present in the crystal, to study their properties, to know the mechanical, electrical and thermal properties of the crystal. By characterization technique we were able to know the physical and chemical properties of the crystal which is used to improve the quality of the crystal. Following are the characterization techniques which is used to study the grown crystal.

- Powder X-Ray Diffraction (PXRD)
- Fourier Transform Infrared Spectroscopy(FTIR)
- Ultra Violet- Visible Spectroscopy (UV-Vis)
- Non-Linear Optics (NLO)
- Thermal Analysis (TA)

3.2 METHODOLOGY

Potassium Dihydrogen Phosphate (KDP) is selected with the additives as Succinic acid, L-Ascorbic acid and DL-Malic acid As KDP is a well known non-linear crystal, it is interested to study the role of additives such L-Ascorbic acid , DL-Malic acid and Succinic acid done with KDP crystal, was done with the KDP crystal. The additives for KDP has chosen because of their additives in food, the vitamins present in fruits,etc., L-Ascorbic acid has enormous amount of Vitamin-C which is a water soluble vitamin and it is also found in citrus and other fruits. DL-Malic acid is an organic compound and also dicarboxylic acid which is contributed in sour taste of fruits and vegetables and also a food additive. Succinic acid is also presents in many food, chemicals and pharmaceutical industries.

3.3 PHYSICAL & CHEMICAL PROPERTIES OF KDP & THEIR ADDITIVES

These are the following physical and chemical properties of KDP and the additives such as Succinic Acid, L-Ascorbic Acid and DL-Malic acid.

3.3.1 PHYSICAL AND CHEMICAL PROPERTIES OF KDP

Molecular Formula : KH_2PO_4

Molecular Weight : 136.086

Colour/ form : Colorless crystals or white granular powder

Crystal System : White tetragonal crystals

Odor : Odorless

pH : 4.4 to 4.7

Solubility : Freely soluble in water and insoluble in ethanol

Melting Point :253^{0}C

Density :2.34 g/ cm^3

3.3.2 PHYSICAL AND CHEMICAL PROPERTIES OF L-ASCORBIC ACID

Molecular Formula : $C_6H_8O_6$

Molecular Weight : 176.12

Colour/ form : White to pale yellow, odourless crystalline powder

Crystal System : Monoclinic system

Odor : Odorless

pH : pH= 3(5 mg/mL); pH=2(50 mg/ mL)

Solubility :Insoluble in ether, chloroform, benzene, petroleum ether, oils,
Fats, fat solvents.

Melting Point : 191^0C

Density : $1.65 g/cm^3$

3.3.3 PHYSICAL AND CHEMICAL PROPERTIES OF DL-MALIC ACID

Molecular Formula : $C_4H_6O_5$

Molecular Weight : 138.06

Colour/ form : Colorless crystals

Crystal System : Triclinic sytem

Odor : Characteristic

pH : pH of a 0.001% aqueous solution is 3.80, 0.1% solution is 2.80, 1.0% solution is 2.34

Solubility : Highly soluble in methanol, ethanol, acetone, ether and other Polar solvents.

Melting Point : 131^0C

Density : 1.601 g/cm^{3}at 20^0C

Boiling Point : Decomposes at >225^0C

3.3.4 PHYSICAL AND CHEMICAL PROPERTIES OF SUCCINIC ACID

Molecular Formula : $C_4H_6O_4$

Molecular Weight : 118.09

Colour/ form : White minute monoclinic prisms

Crystal System : Triclinic or Monoclinic Prisms

Odor : Odorless

pH : 2.7 (0.1 molar aqueous solution)

Solubility : Soluble in ethanol, ethyl ether, acetone, methanol , slightly Soluble in deuterated dimethyl formamide, insoluble in toluene, Benzene.

Melting Point : 188^{0}C

Density : 1.572 at 25^{0}C

Boiling Point : 235^{0}C.

3.4 POWDERED XRD (PXRD)

X-ray is an important technique which is useful to characterize the crystal. It is mainly used for phase identification of a crystalline material and unit cell dimensions of the crystals are also known where the materials are finely ground, homogenized and average bulk composition are also determined.

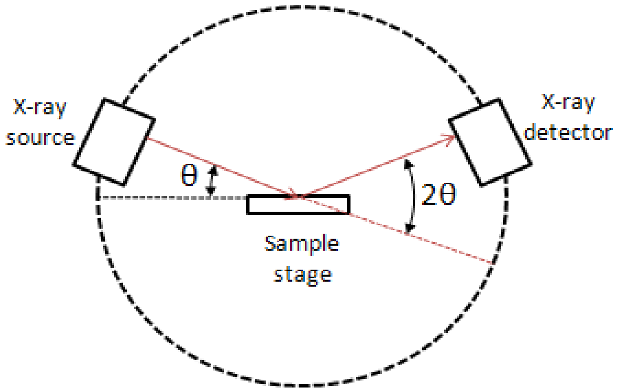


Fig. 3.1 Powdered X-Ray Diffraction.

The fundamental principles behind powdered XRD is based on the elastic scattering of X-rays. The range is of long range order and the scattering of crystals gives the information on dynamical theory of diffraction. If the wavelength from the scattered crystal did not change as the XRD-photons produced did not lose energy, they are called as elastic scattering. In inelastic scattering, there will be some transfer of energy with different wavelength than incident X-rays. By measuring the diffraction pattern to deduce the distribution of atoms in a material [47].

3.4.1 BRAGG'S LAW

The peaks in XRD are determined by Bragg' law which is $2d \sin\theta = n\lambda$ in which d is the interplanar distance, θ is the scattering angle, n is an integer which is the order of diffraction peak and λ is the wavelength of the x-ray. Powdered XRD is preferred in polycrystalline or powdered solid samples. It can be also used to characterize heterogeneous solid mixtures and a common method for determining strains in crystalline materials. From the name PXRD, we can find that it exists in a powder form, consisting of fine grains of single crystalline material and the crystalline domains are randomly oriented in the sample.

3.4.2 APPLICATIONS OF PXRD

- PXRD is majorly used in identifying the crystalline materials which are not common to us such as minerals and unknown compounds.
- Optically determinant materials can also be identified such as clays.
- We can also examine the samples purity and unit cell dimensions.

3.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR is a great tool for identifying the functional groups where different types of chemical bonds are identified in a molecule by producing infrared spectrum which is like a molecular "finger print". It is a good tool for identifying organic and few inorganic material. The absorption of various infrared wavelengths can also be measured and the molecular component with the structures are identified.

The working process of FTIR includes a source, interferometer, sample, and a detector. The source used in FTIR can be black-body source, when the beam passes through the aperture, the energy is emitted and it controls the amount of energy. In the interferometer, the beam enters and spectral encoding takes place. The beam enters the sample compartment, so that it can be transmitted or reflected off the surface and specific frequencies of energy are aborted. The beam finally enters the detector and special interferogram signal are measured [48].

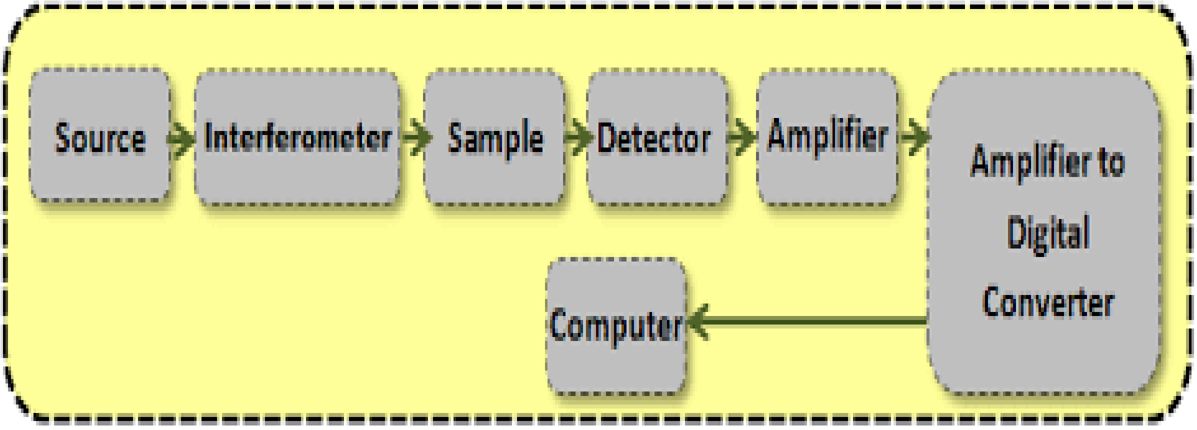


Fig. 3.2 Fourier Transform Infrared Spectroscopy

In FTIR, the radiation contains all IR wavelengths and they can split into fixed length and variable length where the variable length is called as movable mirror. The distances varying between the pathlengths may result in constructive or destructive interference. Constructive interference refers to the phase difference between the waves which is an even multiple of π (180°). Destructive interferencetakes place when waves come together in such a manner that they completely cancel each other out. There will be an variation in intensities which is called as interferogram. With the help of interferogram, the fourier transform converts the time domain into frequency domain and the piston adjusts the position of the mirror. Passage of the IR radiation through the sample initiates the compound to broad band of energies. In FTIR, monochromator is not used and these devices are used to select radiation of single wavelength or energy [50].

3.6 UV-SPECTROSCOPY

UV- Spectroscopy is used to study the optical properties of the materials where ultraviolet and visible spectroscopy comes under electronic spectroscopy. When a molecule absorbs light of certain wavelength, electronic transitions can occur as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ and there will be only compounds with π electrons or non bonding electrons for producing UV specta. Silver chloride when exposed to sunlight the colour changes to black because of UV radiation as sun is the natural source of UV radiation. Therefore four methods were adopted in UV radiation such as

- Photographic plates will change the colour when it is exposed to UV radiation.

- The process by which certain substance emit visible light when exposed to UV is called fluorescence.
- The process by which the substances are continuously emitting visible light even when we take of UV is called phosphorescence.
- Photo electric effect also plays an important role in UV radiation as the light source emit electrons [47].

3.6.1 UV AND ITS APPLICATIONS

The UV functions very effectively when a beam of light coming from visible or UV light is separated either by a prism or diffraction grating. The beam passes through a transparent container to study the transparent solvent and the other beam passes through an identical cuvette where only one solvent is present. The intensities of the light are measured and the UV region is scanned from 200-400 nm and the visible is from 400-800 nm.

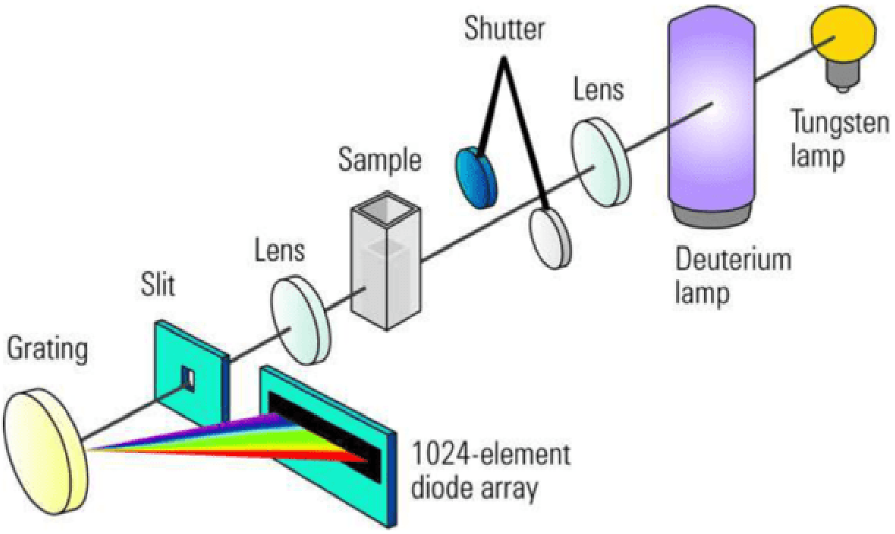


Fig. 3.3 Schematic Diagram of UV Spectroscopy

APPLICATIONS

- Dissociation constant of acids and bases can be found by UV spectroscopy.
- UV absorption is generally used for qualitative determination of compounds absorbed by UV.
- UV method is one of the best method for defecting impurities in organic compounds
- This method can characterize the compounds which absorb UV radiation.

- This method can also used to study the kinetics of reaction [47].

3.7 NON LINEAR OPTICAL STUDIES (NLO)

Non-linear optics deals with the study of interaction of intense electromagnetic fields where the materials produced are modified with respect to difference in input fields in phase, frequency and amplitude. To modify the optical properties of a material system, we need only one laser light and second harmonic generation is frequently taken. The response of an optical field will be non- linear in nonlinear optics phenomenon, so that there will be an increase as the square of intensity of the applied laser light.

Polarization, which is an important phenomenon comes under NLO properties. In uniaxial crystals, a special direction exists are called optic axis and the plane containing optic axes and wave vector of light wave is called principle plane. Light beam whose polarization is normal to the principal plane is known as ordinary beam or an o- beam and the polarized beam is called extra-ordinary beam or e-beam. There also exists a difference between an ordinary and extra-ordinary beam which is called as birefringence. Uniaxial crystals are transmissive optical elements in which the refractive index of one crystal is different from the other two crystals.

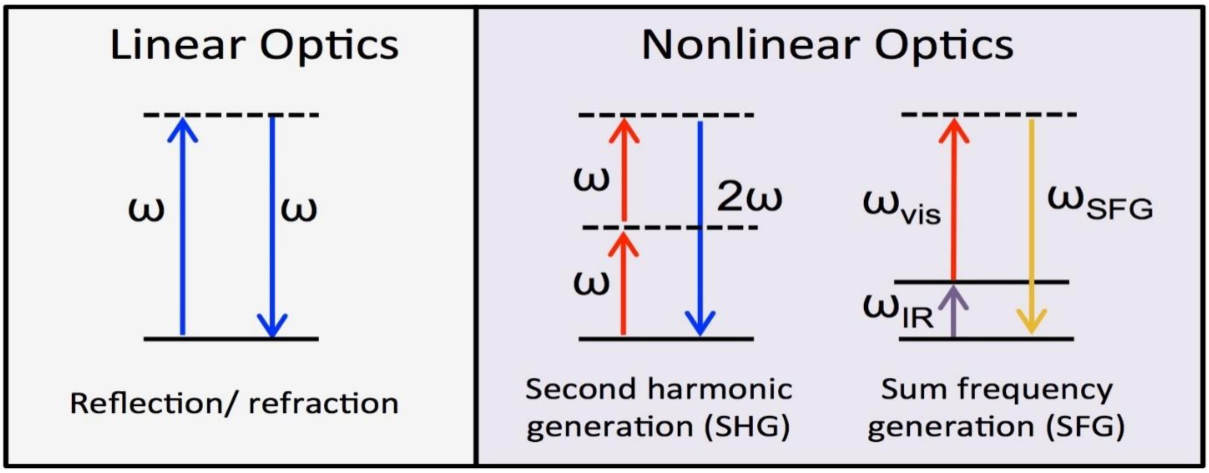


Fig. 3.4 Difference between linear and non-linear optics

Phase matching bandwidth plays an important role in NLO Fundamental wave depletion which is called as Non-linear regime were also observed in non-linear optics. NLO applications can be mainly used to study the second and higher (it can be up to sixth) optical harmonics. It involves wide- aperture neodymium glass laser radiation, generation of optical harmonics of other lasers such as ruby gas, semiconductors, sum frequency generation, difference frequency generation, parametric light oscillation, picosecond continuum generations. Second harmonic generation is a non-linear optical process in which the two photons of the same frequency interact with a non-linear material, are combined and generate a new photon with twice the energy of the initial photons which conserves the coherence of the excitation [49].

3.8 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

It is also called as DSC shortly. It is one of the best thermal analysis technique, in which the physical property of a substance is measured to control temperature program. This type of characterization gives the brief information on thermal properties of various biological macromolecules and extracts which is a highly sensitive technique. The term thermal analysis are applied where some physical parameter of the system determined or recorded as a function of temperature. It can also determine the physical, chemical properties of polymers, electronic circuit board, geological materials and coal [36].

3.8.1 WORKING OF DSC

It is a thermo-analytical method where the calorimeter measures the heat passes into or out of sample whereas differential calorimeter measures the heat of a sample relative to a reference and heats the sample at linear temperature ramp. DSC was used to measure the difference in amount of heat required to increase the temperature and reference was used to measure as the function of temperature. The principle of this technique says that when a sample undergoes a physical transformation such as a phase transition, the reference need more or less heat needed to maintain the same temperature where the process depends on endothermic or exothermic [48].

3.8.2 DSC INSTRUMENTS

There are four types of DSC instrument used that are

- Heat flux DSC.
- Power compensated DSC.
- Modulated DSC.
- Pressure DSC.

The difference in heat flow into the sample and the reference were measured using heat flux DSC and the main assembly of DSC cell is cylindrical or silver heating black and chromel constant thermocouples are used to determine the differential temperatures.There are various types of heat flux DSC is available and they are HF-the cylinder measuring system, the turret-type measuring system.

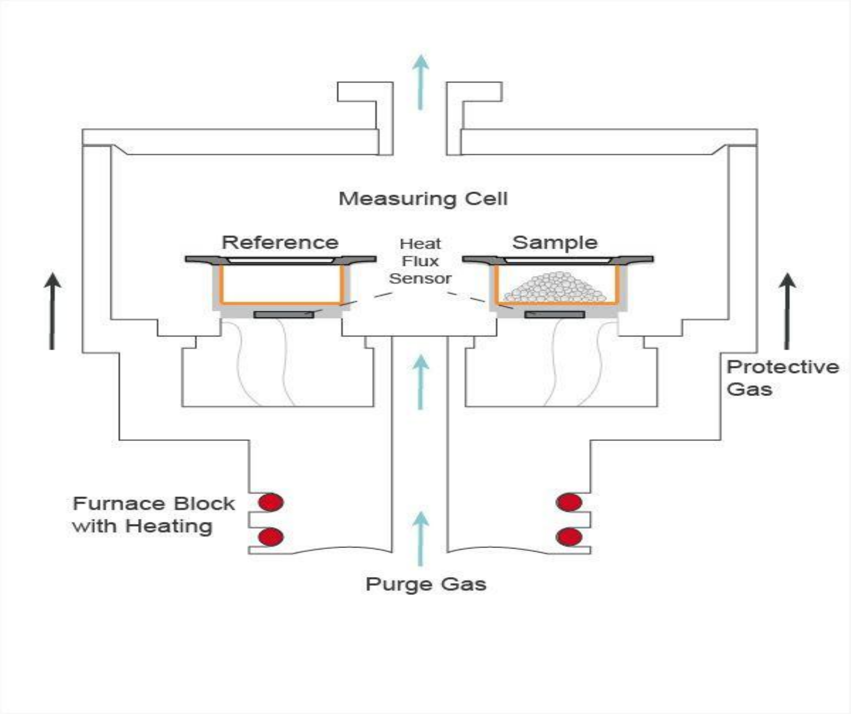


Fig. 3.5 Schematic Diagram of DSC instruments

In power compensated DSC, we can measure the temperatures of the sample and reference which they are kept equal to each other where the temperature can increase or decrease linearly.We can measure the power needed to maintain the sample temperature equal to the reference temperature. All PC DSC has same basic principles and the special PC DSC is called photo DSC.

In modulated DSC, they use the same heating and cell arrangement as the heat. This is one of the new technique found in 1993.We can separate the overlapping events in DSC scans. MDSC is a valuable extension of conventional DSC.

In pressure DSC, the samples are submitted to different pressures, which allows the characterization of substances at the pressure of the process to distinguish the over lapping peaks. There are various applications takes place such as pressure sensitive reactions, evaluation of catalysts, resolution of over lapping transitions [48].

3.9 MOLECULAR STRUCTURE OF KDP AND THEIR ADDITIVES

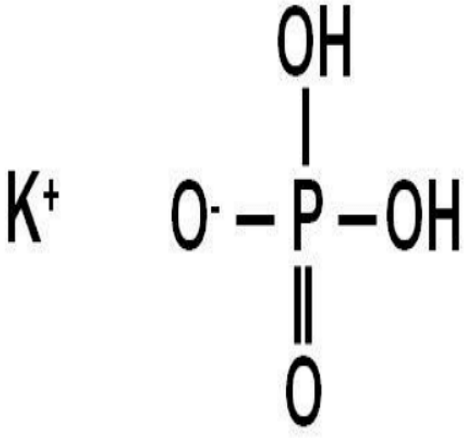


Fig. 3.6 Molecular Structure of KDP

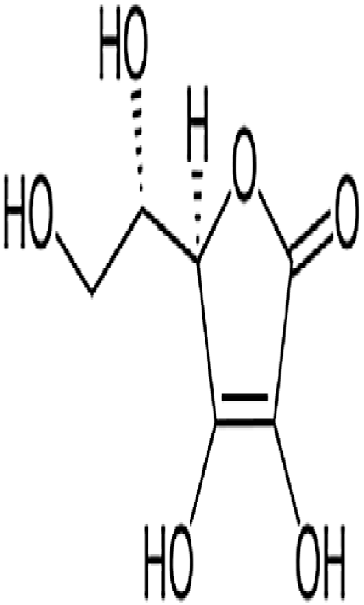


Fig. 3.7 Molecular Structure of L-Ascorbic acid

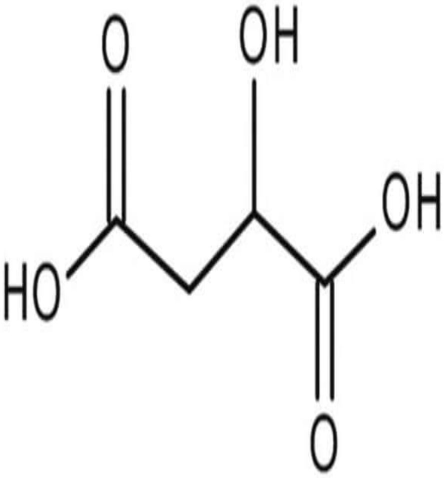


Fig. 3.8 Molecular Structure of DL-Malic acid

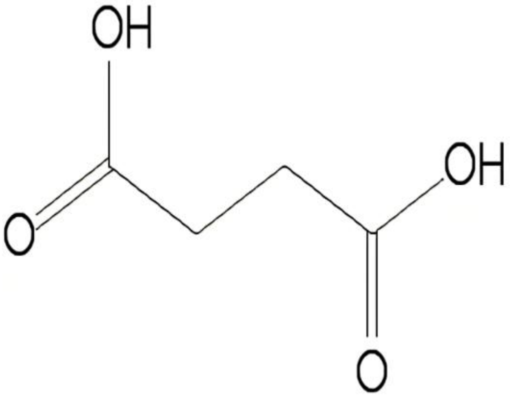


Fig. 3.9 Molecular Structure of Succinic acid

RESULTS AND DISCUSSION

CHAPTER-4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

In a wide range of materials available for industrial applications, potassium dihydrogen phosphate (KDP) single crystals seek enormous attention owing to optically active, structural diversity, high optical homogeneity, enhanced charge mobility, short photonic response time and large nonlinear coefficient. Inhabiting the foresaid features the KDP single crystals are readily demanded in hi-tech fields for designing optical switching, data storage, frequency conversion, laser assisted remote sensing, high speed optical information processing and photonic devices. In the present work, pure KDP and KDP added with Succinic acid, L-Ascorbic acid and DL-Malic acid crystals are grown. The grown crystals are characterized and results pertaining to that are discussed in this chapter.

4.2 SYNTHESIS OF THE COMPOUNDS USING SOLUTION METHOD

KDP and their additives were added in 1:1 ratio to obtain saturation solution by slow evaporation technique. The process is carried out with the help of a magnetic stirrer, 100 ml of distilled water, a magnetic pellet and a 100ml beaker. The solute KDP and their additives are added alternately, so that the material gets completely soluble in distilled water. The saturated solution is the basis for growing a crystal. The saturated solution is filtered with the help of a funnel and Whatman filter paper. The filtration process took place for about 30 minutes and the filtered solution is covered with perforated sheet with the solution present in the beaker. As this is a slow evaporation method, the filtered solution was allowed to evaporate slowly by making small holes in the upper part of the sheet. The beaker with the filtered solution is allowed to evaporation for about two weeks.

A] Pure KDP

Using powdered KDP (Analytical Grade), crystals are grown. The powder is dissolved in 100 ml of deionized water at 40^0 C temperature. The solution is stirred continuously until it is saturated. After reaching saturation, the solution is filtered and kept in a beaker for growth. Seed crystal is harvested and it is shown in Plate 4.1.

B] L-Ascorbic acid added KDP

The powders are dissolved in 100 ml of deionized water at 40^0 C temperature. L-Ascorbic acid and KDP were added alternatively in the ratio of 1:1. The solution is stirred continuously until it is saturated. After reaching saturation, the solution is filtered and kept in a beaker for growth. Seed crystal is harvested and it is shown in Plate 4.2.

C] DL-Malic acid added KDP

The powders are dissolved in 100 ml of deionized water at 40^0 C temperature.DL-Malic acid and KDP were added alternatively in the ratio of 1:1. The solution is stirred continuously until it is saturated. After reaching saturation, the solution is filtered and kept in a beaker for growth. Seed crystal is harvested and it is shown in Plate 4.3.

D] Succinic acid doped KDP

The powders of KDP and Succinic acid are dissolved in 100ml of deionized water at 40^0 C temperature.Succinic acid and KDP were added alternatively in the ratio of 1:1. The solution is stirred continuously until it is saturated. After reaching saturation, the solution is filtered and kept in a beaker for growth. Seed crystal is harvested and it is shown in Plate 4.4.

The grown crystals are taken for the following characteristic studies such as

- Powder X-Ray Diffraction (PXRD)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Ultra Violet- Visible Spectroscopy (UV-Vis)
- Thermal Analysis (TA)
- Non-linear optical studies (NLO)

4.3 Powder X-Ray Diffraction pattern of grown crystals

PXRD analysis was carried out for pure KDP by XRD-X-Pert Pro Panalytical with CuKα (λ= 1.5460). The sample was scanned at 2ϴ, the hkl values are indexed and the pure KDP crystal belongs to tetragonal system. The hkl values of pure KDP are (200), (112), (220), (312). The plane (200) has high intensity compared to other peaks in KDP.The hkl values of Succinic acid added KDP are (011), (200) ,(021) and (312). The planes such as (200), (301) and (312) are same in KDP doped Succinic acid and pure KDP. The hkl values of L-Ascorbic acid added KDP are (002), (112) and (202). The plane (112) in L-Ascorbic Acid added KDP matches with pure KDP. The hkl values of DL-Malic acid added KDP are (200), (112), (220), (301), (312) and (420). The planes such as (200), (112), (220), (301), (312) in DL-Malic Acid added KDP matches with pure KDP.

4.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

1] In Pure KDP, the presence of functional groups in the pure and doped KDP crystals was analyzed using FT-IR spectral analysis. The FTIR used here for analysis is **FTIR - SHIMADZU (Miracle 10).**The wavenumber and the corresponding vibrational assignments are listed in Table 4.1. In pure KDP, OH stretching takes place at the range of 3603.03 cm^{-1}, P-O-H stretching at 2337.72cm^{-1}, OH bending in hydrates at 1527.62cm^{-1}, P=O stretching at 1280.73cm^{-1},HPO_4^{2-} at 1056.99cm^{-1}, Hypophosphites at 810.10cm^{-1}, P-O-P linkage at 686.66cm^{-1}, $H_2PO_4^-$ at 648.08cm^{-1} , OH-P-OH bending in PO_4vibrations at 648.08cm^{-1}, P^+-O^- deformation in phosphates at 555.50 cm^{-1}, 524.64 cm^{-1}, 486.06 cm^{-1}and 462.92 cm^{-1}, PO_4 vibrations at 432.05 cm^{-1}.

2] In KDP doped L-Ascorbic acid, OH stretching in hydrates takes place at the range of 3410.15 cm^{-1}, P-O-H stretching at 2314.58cm^{-1}, C=O (S) stretching at 1751.36cm^{-1}, 1658.78cm^{-1}, OH bending in hydrates at 1527.62cm^{-1}, (P=O stretching) H bonding very strong at 1311.59cm^{-1}, 1265.30cm^{-1}, HPO_4^- at 1111.00cm^{-1}, 1026.13cm^{-1}, P-O-P stretching at 987.55cm^{-1}, Hypophosphites at 864.11cm^{-1}, 817.82cm^{-1}, P-O-P linkage at 756.10cm^{-1}, 686.66cm^{-1},$H_2PO_4^-$ at 648.08cm^{-1}, P^+-O^- deformation in phosphates at 555.20 cm^{-1}, 524.64 cm^{-1}, PO_4 at 455.20 cm^{-1}, 432.05 cm^{-1} in cm^{-1}.

3] In KDP doped DL-Malic acid, OH stretching takes place at the range of 3842.20 cm^{-1}, OH stretching at 3603.03cm^{-1}, P-O-H stretching takes place at 2306.86cm^{-1}, OH-bending in hydrates at 1689.64cm^{-1}, 1527.62cm^{-1}, (P=O stretching) H bonding very strong at 1273.02cm^{-1}, Hypophosphites at 864.11cm^{-1}, 810.10cm^{-1}, P-O-P linkage at 686.66cm^{-1}, $H_2PO_4^-$ at 648.08cm^{-1}, P^+-O^- deformation in phosphates at 578.64cm^{-1}, 547.78cm^{-1}, 486.06cm^{-1}, PO_4vibrations at 455.20 cm^{-1}, 416.62 cm^{-1}.

4] In KDP doped Succinic acid, OH stretching in hydrates takes place at the range of 3695.61 cm^{-1}, OH bending in hydrates at 1689.64cm^{-1}, 1527.62cm^{-1}, P-OH- deformation in acid salts at 1411.89cm^{-1},1303.88cm^{-1},P^+-O^-at 1195.87cm^{-1}, P-O-P stretching at 894.97cm^{-1}, Hypophosphites 802.39cm^{-1}, P-O-P linkage at 686.66cm^{-1}, $H_2PO_4^-$ at 648.08cm^{-1}, P^+-O^- deformation in phosphates at 547.78cm^{-1},PO_4 vibrations at 424.34 cm^{-1}.

Table 4.1 FTIR peaks assignment values of pure and doped KDP crystals

Vibrational frequencies (cm^{-1})				**Bond assignment**
Pure KDP	**KDP added with L-Ascorbic acid**	**KDP added with DL-Malic acid**	**KDP added with Succinic acid**	
3603.03	3410.15	3842.20, 3603.03	3695.61	OH stretching in hydrates
2337.72	2314.58	2306.86	_____	P-O-H stretching
_____	1751.36, 1658.78	_____	_____	C=O (S)
1527.62	1527.62	1689.64, 1527.62	1689, 1527.62	OH bending in hydrates
_____	_____	_____	1411.89, 1303.88	P-OH deformation in acid salts
_____	1311.59, 1265.30	1273.02	_____	(P=O stretching) H bonding very strong
1280.73	_____	_____	_____	P=O stretching
_____	_____	_____	1195.87	P^+-O^- stretching mode in phosphate ions
1056.99	1111.00, 1026.13	_____	_____	HPO_4^{2-} (S)
____	987.55	_____	894.97	P-O-P stretching
810.10	864.11, 817.82	864.11, 810.10	802.39	Hypophosphites ion (O=P-OH)
686.66	756.10, 686.66	686.66	686.66	P-O-P Linkage
648.08	648.08	648.08	648.08	$H_2PO_4^-$
601.79	_____	____	_____	OH-P-OH bending in PO_4 vibrations
555.50,524.64, 486.92, 462.92	555.50,524.64	578.64, 547.78	547.78, 486.06	P^+-O^- deformation in phosphates
432.05	455.20, 432.05	455.20. 416.62	424.34	PO_4 vibrations

4.5 ULTRA VIOLET RADIATION- VISIBLE (UV-VIS) SPECTRUM

The instrument used here in UV is Biospec Nano Spectrophotometer- Shimadzu/206-26300-48 in the wavelength range between 200 to 800nm. The transmittance curves show Pure KDP is 97% transparent , KDP doped with L-Ascorbic acid is 95% transparent , KDP doped with DL-Malic acid is 95% transparent , KDP doped with Succinic acid is 97% transparent. KDP doped L-Ascorbic has more transmittance than Pure KDP, KDP doped DL-Malic acid, KDP doped Succinic acid. KDP doped Succinic acid has less transmittance compared with other three is shown in the Fig. 4.3. Bandgap energies are calculated using Table Plot as shown in Fig. 4.8 to 4.11 and listed in Table 4.2. Bandgap energies are found to be slightly increased in KDP+ DL-Malic acid and KDP+ Succinic acid.

Table 4.2 Bandgap energies

Grown crystal	**Band gap (eV)**
Pure KDP	5.32
KDP+L-Ascorbic acid	4.49
KDP+DL-Malic acid	5.39
KDP+ Succinic acid	5.45

4.6 THERMAL ANALYSIS (TA): DSC&TGA

The instruments used for Differential Scanning Calorimetry (DSC) andThermo Gravimetric Analysis(TGA) studies is NET ZSCH STA 449F3 STA449F3A-0929-M.The heating was done at a rate of 27^0 C/20.0 (K/Min)/ 500^0 C. In TGA, the decomposition point was observed as 230.28^0 C in pure KDP, 185.36^0 C in KDP doped L-Ascorbic acid, 190.03^0 C in KDP doped DL-Malic acid, 180.55^0 C in KDP doped succinic acid. In DSC, Endothermic peak was observed as 237.43^0 C in pure KDP, 190.03 ^{0} C in KDP doped L-Ascorbic acid, 239.76^0 C in KDP doped DL-Malic acid, 17.45^0 C in KDP doped Succinic acid.These are listed in Table 4.3.

Table 4.3 Decomposition point & Endothermic peak

Grown crystal	**Decomposition Point(TGA)**	**Endothermic peak(DSC)**
Pure KDP	230.28	237.43
KDP+L-Ascorbic acid	185.35	190.03
KDP+DL-Malic acid	190.027	239.76
KDP + Succinic acid	180.54	179.44

4.7 NON-LINEAR OPTICAL STUDIES (NLO)

The NLO property is analysed by the help of Kurtz-Perry powder technique. The single crystals were made into powder form and were packed in an elusion tube and exposed to Nd: YAG laser radiation with a wavelength of 1064 nm. Second Harmonic Generation was confirmed by the emission of green light with a wavelength of 523 nm from the sample.SHG efficiency of the grown crystals are listed in the Table 4.4. The efficiency is found to be increased for the KDP doped with DL-Malic acid crystals.

Table 4.4 SHG efficiency of the grown crystals

Grown crystals	**I_{SHG} (mV)**
Pure KDP	20
KDP doped L-Ascorbic Acid	15
KDP doped DL-Malic Acid	38
KDP doped Succinic Acid	16

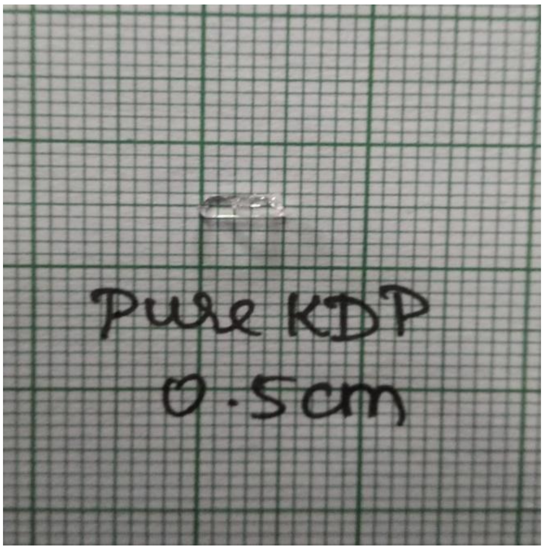


Plate 4.1 Photograph of Pure KDP (0.5 cm)

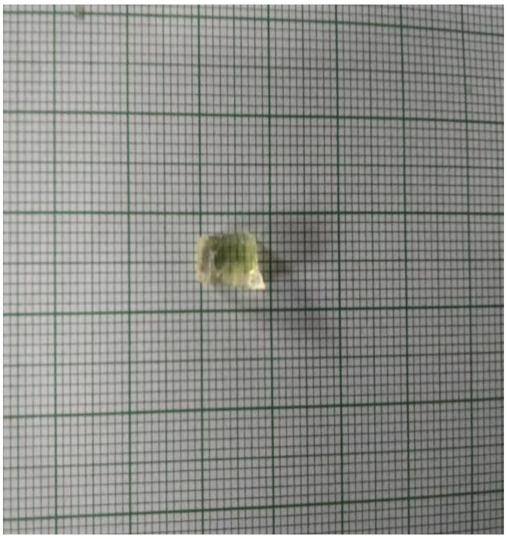


Plate 4.2 KDP doped L-Ascorbic acid (0.8 cm)

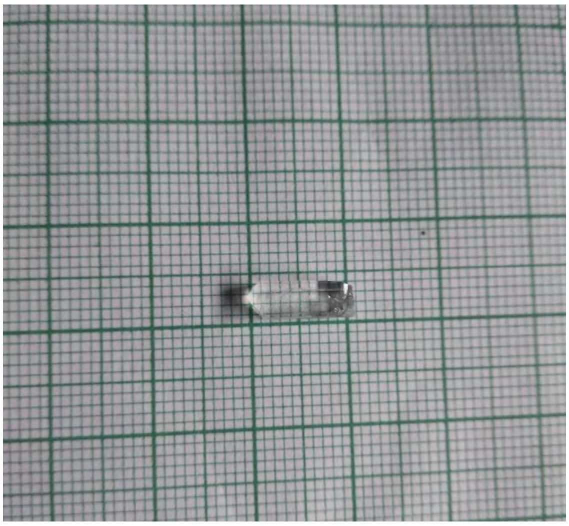


Plate 4.3 Photograph of KDP doped DL-Malic acid (1.1 cm)

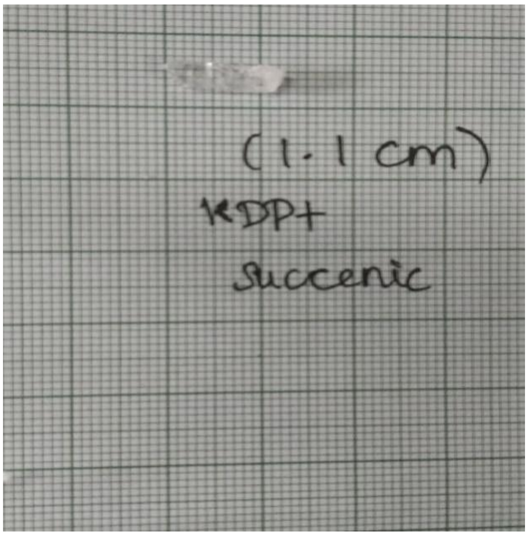


Plate 4.4 Photograph of KDP doped Succinic acid (1.1 cm)

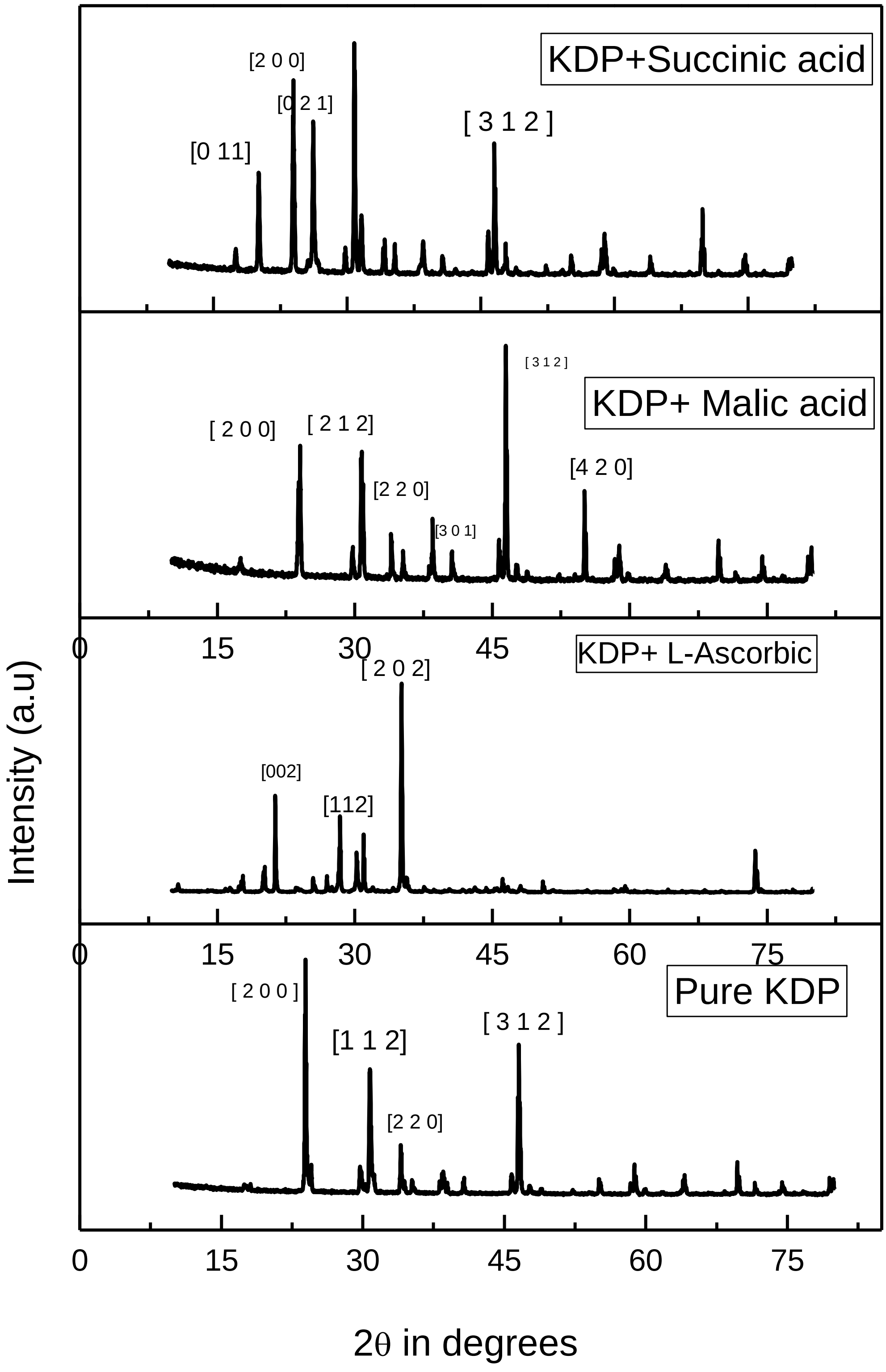


Fig. 4.1 PXRD pattern of grown crystals

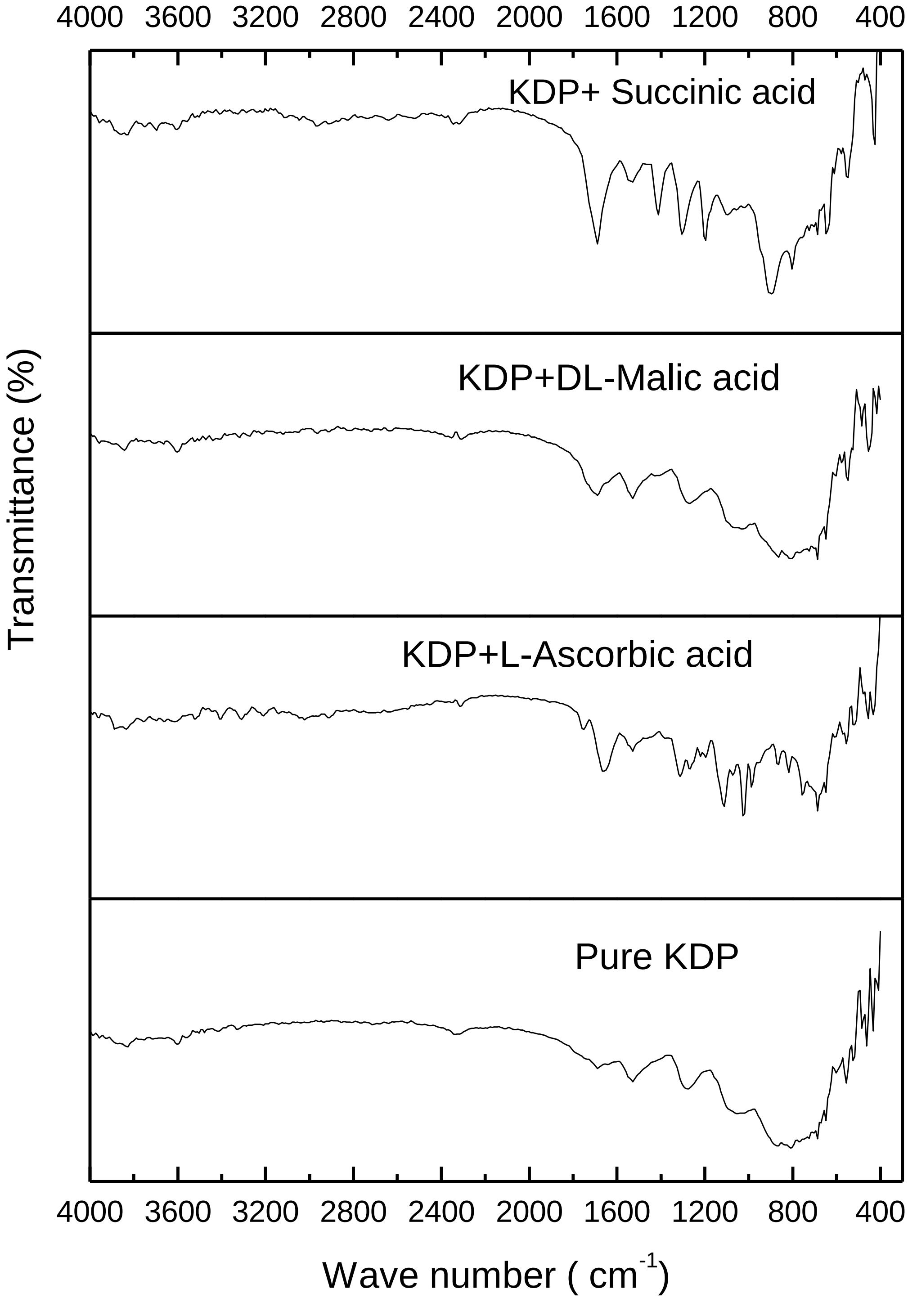


Fig. 4.2 FTIR spectra of the grown crystals

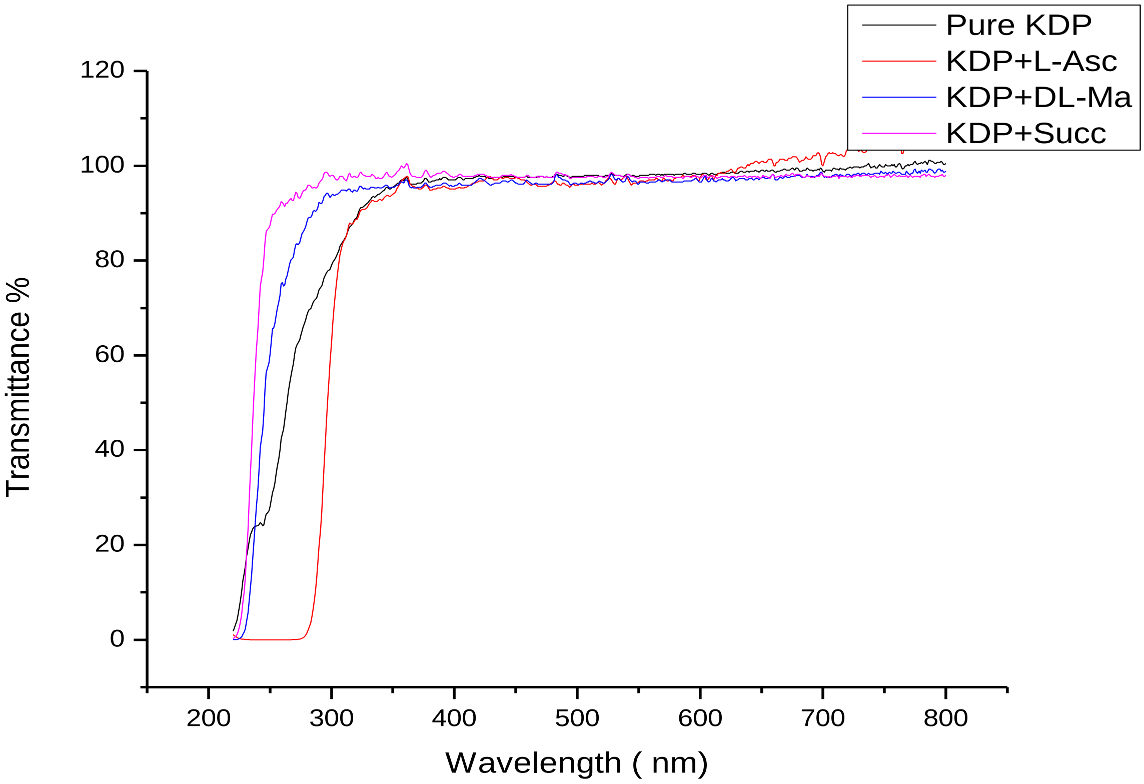
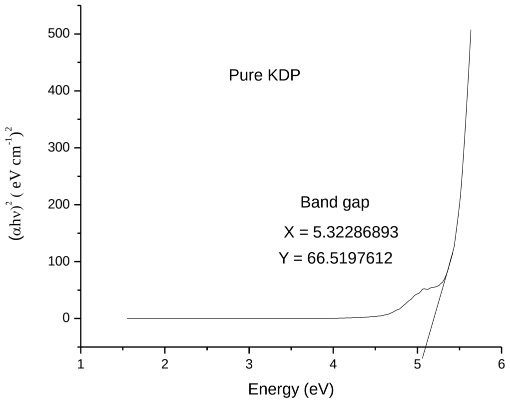


Fig.4.3 UV-Vis Transmittance of the grown crystals



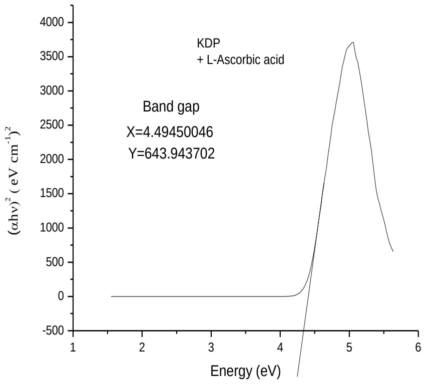
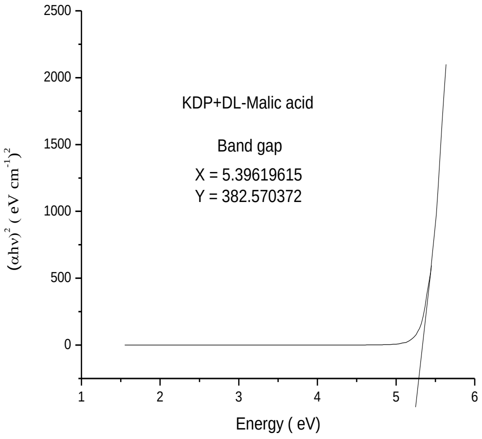


Fig. 4.4 Bandgap energy of Pure KDP **Fig. 4.5 Bandgap energy of**

KDP doped L-Ascorbic Acid



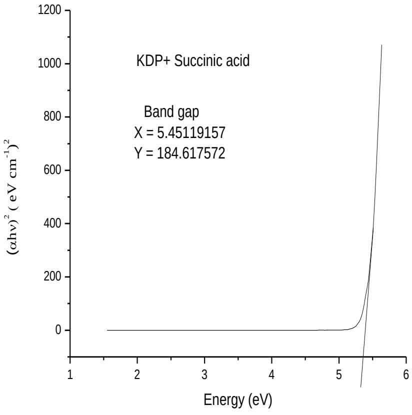


Fig. 4.6 Bandgap energy of KDP doped DL-Malic acid

Fig. 4.7 Bandgap energy of KDP doped Succinic acid

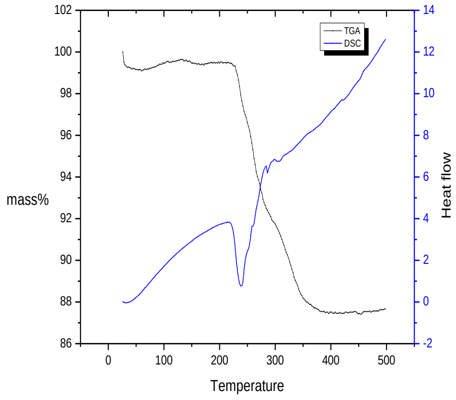


Fig. 4.8 DSC & TGA of

pure KDP

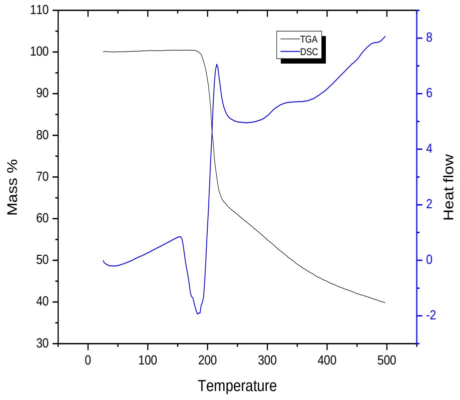


Fig. 4.9 DSC & TGA of

KDP doped L-Ascorbic acid

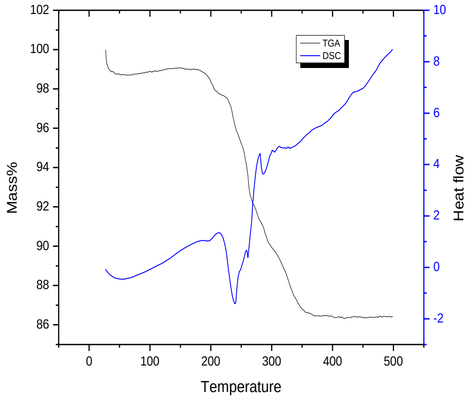


Fig. 4.10 DSC & TGA of

KDP doped DL-Malic acid

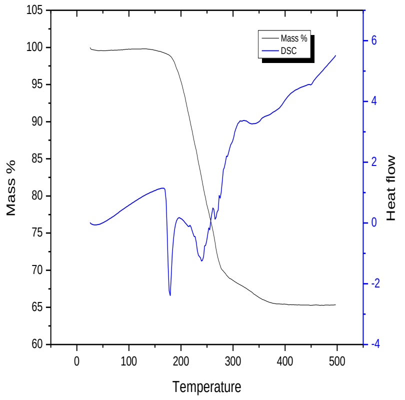


Fig. 4.11 DSC & TGA of

KDP doped Succinic acid

SUMMARY AND CONCLUSION

CHAPTER-5

SUMMARY AND CONCLUSION

KDP is a well -known NLO crystal. It was doped with L-Ascorbic Acid, DL-Malic Acid and Succinic Acid and was successfully grown by a slow evaporation process. The PXRD spectrum showed good similarity with pure and doped KDP crystals.The FTIR spectrum confirmed the presence of functional groups in pure KDP and their additives. Optical behaviour shows good transparency in KDP doped L-Ascorbic Acid compared with others. The band gap energy of KDP doped DL-Malic Acid, Succinic Acid and Pure KDP are well correlated with each other and KDP doped L-Ascorbic Acid has less energy when compared with other dopants and pure KDP. TGA studies explained the weight loss in pure KDP and KDP dopants. DSC studies explained the phase transition occurred in Pure KDP and KDP dopants. The SHG efficiency of KDP doped DL-Malic Acid has increased when compared with pure KDP and other dopants.

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