Characterisation of L-Ascorbic Acid, DL-Malic Acid and Succinic Acid doped Ammonium Dihydrogen Phosphate Crystals

by

MONISHA. M

(20PPH011)

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 Department

27/5/2022

Signature of the
Supervisor

ACKNOWLEDGEMENT

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M. Monisha
27/05/22
M.MONISHA

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CHAPTER I

INTRODUCTION

1.1. Introduction

A crystal or crystalline solid is a solid material whose constituents (such as atoms, molecules, or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. In addition, macroscopic single crystals are usually identifiable by their geometrical shape, consisting of flat faces with specific, characteristic orientations. The scientific study of crystals and crystal formation is known as crystallography. The process of crystal formation is called crystallization or solidification [1].

1.2. Types of solid

The three general types of solids:

- Crystalline solids
- Semi crystalline (Polycrystalline solids)
- Non- crystalline solids (Amorphous)

The three types are distinguished by the size of ordered region within the materials. Order in amorphous solids is limited to a few molecular distances. In polycrystalline materials, the solid is made-up of grains which are highly ordered crystalline regions of irregular size and orientation. Single crystals have long-range order. Many important properties of materials are found to be depending on the structure of crystals and on the electron state within the crystals.

1.2.1. Crystalline solids

A solid is generally said to be crystalline if its constituent elements (atoms, ions, or molecules) are cyclically arranged in three dimensions, or simply if it has a lattice structure. The regularity in the appearance of crystals found in nature or grown in the laboratory led to the belief that crystals are formed by frequent repetition of the building blocks. When a crystal grows in a constant environment, the external geometry of the crystal usually does not change. The shape is the result of the internal arrangement of the constituent particles from which it is made.

1.2.2. Semi crystalline (Polycrystalline) Solids

A solid composed of many crystals that form together as an interlocking mass, randomly oriented and separated by clear boundaries is said to be a polycrystalline solid. In general, the particles of such a solid have no shape associated with the crystal structure, with randomly shaped surfaces rather than well-defined crystal planes. The majority of solids are found in nature such as rocks, sand, metals, salts, etc. However, they can be grown as single crystals under the right conditions. Due to the random distribution of crystals, a polycrystalline solid is isotropic, i.e. their property on an average is same in all directions.

1.2.3. Non-crystalline (Amorphous) Solids

A solid that does not have a mesh or granular structure is called a non-crystalline or amorphous solid. In other words, an amorphous solid is the opposite polarity of a single crystal. Glass and plastic are common examples of these solids. Other common substances include turpentine, pitch, rock candy, and more. The typical feature of these substances is that they do not have a definite melting point. As their temperature increases, they gradually become soft. Their viscosity drops and begins to behave like normal viscous fluids. Observations suggest that an amorphous body can crystallize over time. For example, sugar crystals form in rock sugar after a while. In the same way, glass "ages", i.e. polycrystalline particles are formed in it. When this happens, the glass loses its transparency and becomes brittle [2].

1.3. Crystal

Crystal structure is made up of atoms. A lattice is made up of points. A crystal system is a set of axes. In other words, a structure is an ordered network of atoms, ions, or molecules. Crystal structure is obtained by attaching atoms, groups of atoms or molecules. This structure emerges from the internal nature of the constituent particles to give rise to symmetry patterns. A subgroup of repeating units of an atomic structure is called a unit cell of the structure. A unit cell is the foundation of crystal structure and also explains in detail all crystal structure and symmetry regarding the positions of atoms along with its major axes. The lengths, sides of the major axes, and the angle between the unit cells are called lattice constants or lattice parameters. The unit cell can be defined as the smallest part of the crystal composition. A group of atoms, ions, or molecules, arranged together purely to make up a crystal. The unit cells are structured in three-dimensional space, depicting the giant arrangement of crystalline atoms.

1.4. Types of crystal

A crystal system refers to one of the many classes of crystals, space groups, and lattices. In crystallography terms, lattice system and crystal are associated with each other with a slight difference. Based on their point groups crystals and space groups are divided into seven crystal systems. Seven crystal systems is a classification approach based on their lattice and atomic structure. An atomic lattice is a chain of atoms arranged in a symmetrical pattern. Using the network, it is possible to determine the appearance and physical properties of a rock. These are the seven crystal systems and they are [3],

(i) Cubic
(ii) Triclinic
(iii) Monoclinic
(iv) Orthorhombic
(v) Tetragonal
(vi) Trigonal
(vii) Hexagonal

1.5. History of Crystal growth

The fundamental aspects of crystal growth technology had been derived from early crystallization experiments in 18th and 19th century, with the development of thermodynamics in late-19th century and with the development of nucleation and growth theories and the role of transport phenomena in 20th century. The father of crystal fabrication technology is A.Verneuil with his flame-fusion growth method in 1902. His principles of nucleation and growth control are adapted in later growth methods from melt. The Czochralski method was essentially developed by Teal, Little and Dash. The multidisciplinary nature of crystal growth, epitaxy technology and complex multiparameter processes, and also scaling problem, has impeded the scientific development of this important area. The fabrication technology for crystals and layers were developed in the past 50 years into a multi-billion-dollar industry which delivers basic components for major high-technologies, medical instrumentation, military and space technologies, nuclear physics and so forth. The increased future requirements with respect to size and quality of crystals and layers and with respect to complexity of crystal growth problems necessitate a transition from the so far dominating empirical developments to increasingly scientific approaches [4].

1.6. Introduction to Crystal Growth

To grow a crystal, the basic condition to be attained is the state of super saturation, followed by the process of nucleation. The information of super saturation and nucleation forms the basis of crystal growth. The growth of crystals from liquid and gaseous solutions, pure liquids and pure gases can only occur if some degree of super saturation or super cooling is been first achieved in the system. The attainment of the supersaturated state is essential for any crystallization operation and the degree of super saturation or deviation from the equilibrium saturated condition is the prime factor controlling the deposition process. Crystallization starts with nucleation and control of nucleation is crucial for the control of the number, size, perfection, polymorphism, and other characteristics of crystalline materials. This is particularly true for crystallization in solution, which is an essential part of processes in the chemical and pharmaceutical industries [5].

1.6.1. Nucleation

Nucleation represents the first step in crystallization. Nucleation may be defined as the formation of solid particles of solute capable of further growth. Nucleation may occur spontaneously or it may be artificially induced. These two cases are often referred to as homogeneous and heterogeneous nucleation, respectively. Deciding on whether a system is undergoing homogeneous or heterogeneous nucleation may be quite difficult. Nucleation divides into two types, they are primary and secondary. Primary nucleation refers to all cases of nucleation, homogeneous or heterogeneous, in systems that do not contain crystals.

Secondary nucleation refers to cases where nucleation is induced by crystals present in the supersaturated system [6].

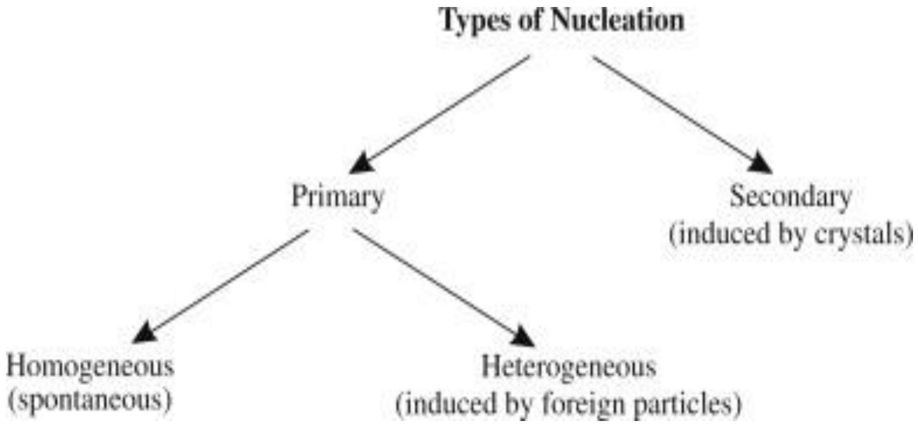

Fig. 1.1. Types of Nucleation

1.6.2. Supersaturation

Supersaturation is non-equilibrium, physical state in which a solution contains more solute than equilibrium solubility allows, given conditions such as temperature and pressure of the system. Supersaturation is also used to describe the level at which the solute concentration exceeds its solubility at given conditions. This is important because it is the driving force for both crystal nucleation and growth. The control of supersaturation is a key to attaining desired product attributes especially final crystal size distribution and phase. Generally, at low supersaturation, crystals can grow faster than they nucleate, resulting in a larger crystal size. At higher supersaturation, crystal nucleation dominates crystal growth ultimately resulting in smaller crystals.

1.7. Techniques for Crystal Growth

The methods of growing single crystals may be classified according to their phase transformation as given below:

Growth from solid; solid → solid phase transformation

Growth from liquid; liquid → solid phase transformation

Growth from vapour; vapour → solid phase transformation [7].

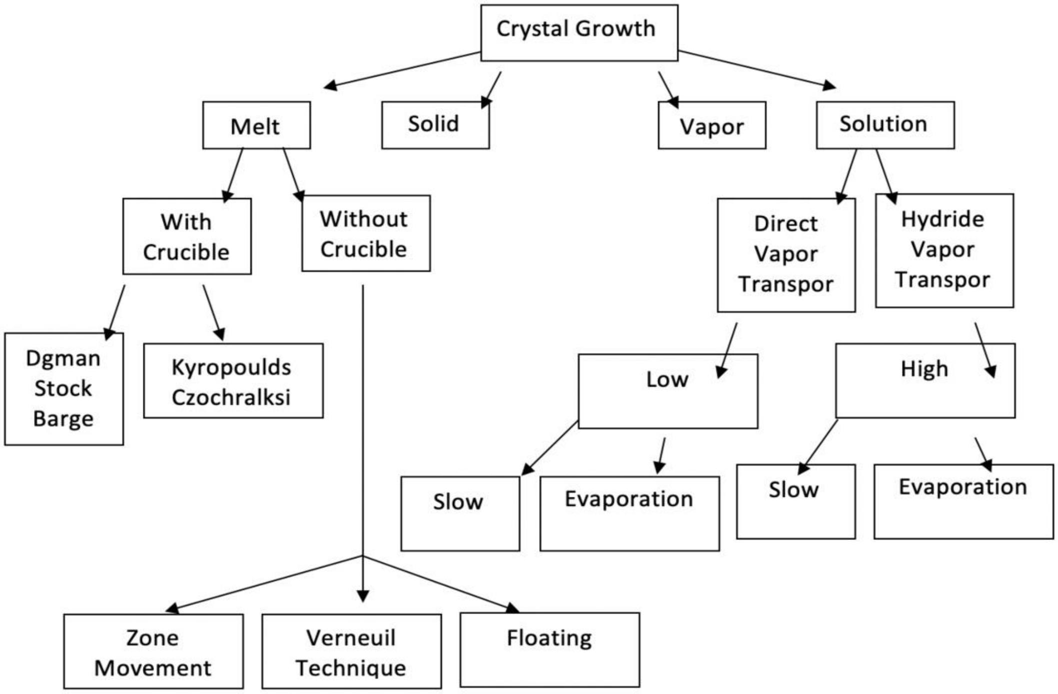

Fig. 1.2. Classification of crystal growth techniques

1.8. Growth from melt

Growth from melt is by far the fastest of the growth methods as its rate does not depend on mass transport process. All materials can be grown in single crystal form from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature. The growth from melt can be further subdivided into the following techniques [8]:

- Bridgman technique
- Czochralski technique
- Kyropoulos technique
- Zone melting and Normal Freezing technique
- Verneuil technique

1.9. Gel Growth

The growth of single crystals in gel is a self -purifying process free from thermal strains which are common in crystals grown from the melt. Crystal growth in gels is a promising technique for growing single crystals of substances which are slightly soluble in water and which cannot be grown conveniently from melt or vapour. The gel method has also been applied to study the crystal formation in urinary calculi and rheumatic diseases. Based on the nature of physical changes and chemical reactions involved in the growth process, gel method can be classified into four categories:

- Chemical reaction method
- Chemical reduction method
- Solubility reduction method
- Complex dilution method

1.10. Growth from Vapour

This is a method by which single crystals and epitaxial layers of high chemical purity and crystalline perfection may be obtained. The thickness and the doping of the layers can be closely controlled and the process can be recycled. Since the growth is slow, the method is not practical for bulk single crystals. Growth from vapour phase may generally be subdivided into two categories:

- Physical vapour transport
- Chemical vapour transport

1.11. Growth from Solution

Materials, which have high solubility and have variation in solubility with temperature, can be grown easily by solution method. There are two methods in solution growth depending on the solvents and the solubility of the solute. They are

- High temperature solution growth
- Low temperature solution growth

1.12. High temperature solution growth

Flux and hydrothermal growths form the category of high temperature solution growth. In the growth of crystals from high temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturation may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a cooler region.

The high temperature crystal growth can be divided into two major categories: first one is growth from single component systems and the second one is that from multi-components .This technique can be used for the crystallization of oxide compounds which generally have high melting points as well as for materials which have phase transitions below the melting point. One major disadvantage of this method is the corrosive nature of the fluxes used, which attack the common furnace materials.

1.13. Low temperature solution growth

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. It is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures and also which undergo phase transformations below melting point. Materials having moderate to high solubility in temperature range, ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method.

The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straight forward equipment design which gives a good degree of control of accuracy of ±0.01 ºC. The main disadvantages of the low temperature solution growth are the slow growth rate in many cases. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low. Three principal methods are used to produce the required supersaturation.

- Slow cooling of the solution
- Slow evaporation of the solvent
- Temperature gradient method

1.13.1. Slow cooling technique

Slow cooling technique is the most suitable method among various methods of solution growth. The main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which crystallization can begin is usually within the range 45 - 75 °C and the lower limit of cooling is the room temperature.

1.13.2. Slow evaporation method

Slow evaporation method is similar to the slow cooling method in view of the apparatus requirements. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.005 °C and rates of evaporation of a few ml /hr. The evaporation techniques of crystal growth have an advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials, having very small temperature coefficient of stability.

1.13.3. Temperature gradient method

Temperature gradient method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are:

- Crystal grows at a fixed temperature
- This method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change.
- Economy of solvent and solute

On the other hand, changes in the small temperature differences between the source and the crystal zones have a large effect on the growth rate. Excellent quality crystals of ferroelectric and piezo-electric materials such as Ammonium dihydrogen phosphate (ADP), Potassium dihydrogen phosphate (KDP) and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method [7].

1.14. Optimizing Solution Growth

The growth of good quality single crystals by slow evaporation and slow cooling techniques require the optimized conditions and the same may be achieved with the help of the following norms:

(i) Solvent selection
(ii) Solubility
(iii) Solution preparation
(iv) Seed preparation
(v) Crystal habit

1.14.1. Solvent selection

A solution is a homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity and the one which gets dissolved in solvent. For a given solute, there may be different solvents.

The solvent must be chosen taking into account the following factors to grow Crystals from solution:

(i) a good solubility for the given solute
(ii) a good temperature coefficient of solute solubility, less viscosity and less volatility
(iii) Less corrosion and non-toxicity cost effective.

It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of surface of the crystal as it grows and the solvent molecules. Solvents commonly used include light water (H_2O), heavy water (D_2O), ethanol, methanol, acetone, carbon tetrachloride, hexane, xylene and many others. Almost 90% of the crystals produced from low temperature solutions are grown by using water as solvent as water has high dielectric constant, stability, low viscosity, low toxicity and abundant availability.

1.14.2. Solubility

Solubility of the material in a solvent decides the amount of material, which is available for growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and lower solubility restricts the size and growth rate of the crystals. Solubility gradient is another important parameter, which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation of the solvent is another option for crystal growth to maintain supersaturation in the solution. Low temperature solution growth is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transfer of growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supersaturation is an important parameter for the solution growth process. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process. The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. Solubility of most substances increases with temperature (the temperature coefficient of solubility is positive) [6].

1.14.3. Solution preparation and crystal growth

For solution preparation, it is essential to have the solubility data of the material at different temperatures. Sintered glass filters of different pore size are used for solution filtration. The clear solution, saturated at the desired temperature is taken in a growth vessel. For growth by slow cooling, the vessel is sealed to prevent the solvent evaporation. Solvent evaporation at constant temperature can be achieved by providing a controlled vapour leak. A small crystal suspended in the solution is used to test the saturation. By varying the temperature, a situation where neither the occurrence of growth nor dissolution is established. The test seed is replaced with a good quality seed. All unwanted nuclei and the surface damage on the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after saturation. Solvent evaporation can also be helpful in initiating the growth.

1.14.4. Seed preparation

Seed crystals are prepared by self-nucleation under slow evaporation from a saturated solution. Seeds of good visual quality, free from any inclusion and imperfections are chosen for growth. Since, strain free refracting of the seed crystal results in low dislocation content, a few layers of the seed crystal are dissolved before initiating the growth. Defects present in an imperfect seed propagate into the bulk of the crystal, which decreases the quality of the crystal. Hence, seed crystals are prepared with care. The quality of the bulk crystal is usually slightly better than that of the seed.

1.14.5. Crystal habit

The growth of a crystal at approximately equivalent rates along all the directions is a prerequisite for its accurate characterization. This will result in a large bulk crystal from which samples of any desired orientation can be cut. Further, such large crystals should also be devoid of dislocation and other defects. These imperfections become isolated into defective regions surrounded by large volumes of high perfection, when the crystal grows with a bulk habit. In the crystals which grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect. Needle like crystals have very limited applications and plate like crystals need to be favourably oriented.

Changes of habit in such crystals which naturally grow as needles or plates can be achieved by any one of the following ways:

(i) Changing the temperature of growth

(ii) Changing the pH of the solution

(iii) Adding a habit modifying agent

(iv) Changing the solvent.

Achievement in this area is of great industrial importance where such morphological changes are induced during crystallization to yield crystals with better perfection and packing characteristics.

1.15. Introduction to Non-Linear Optics

The Nonlinear optics (NLO) is the branch of optics that describes the behavior of light in nonlinear media, that is, media in which the dielectric polarization P responds nonlinearly to the electric field E of the light. This nonlinearity is typically only observed at very high light intensities (values of the electric field comparable to interatomic electric fields, typically 10^8 V/m) such as those provided by pulsed lasers. Above the Schwinger limit, the vacuum itself is expected to become nonlinear. In nonlinear optics, the superposition principle no longer holds. The field of nonlinear optics emerged nearly five decades ago with the development of the first operating laser and the demonstration of frequency doubling phenomena. These milestone discoveries not only created much interest in laser science, but also set the scope for future work in nonlinear optics. The extraordinary growth and development of nonlinear optical materials during the past decade has rendered photonic technologies and indispensable part of our daily life. With the emerging demand for information systems, nonlinear optical materials have been considered as the key elements for the future photonic technologies of optical computing, telecommunications, optical interconnects, high density data storage, sensors, image processing, switching etc.

Nonlinear optics (NLO) deals with the study of the interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude. Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. The process occurs within a nonlinear medium, usually a crystal. Such frequency doubling process is commonly used to produce green light (532 nm) from, for example, a Nd: YAG laser operating at 1064 nm. The light propagated through a crystalline solid, which lacks a centre of symmetry, generates light at second and higher harmonics of the applied frequency. This important nonlinear property of noncentrosymmetric crystals is called second harmonic generation and this phenomenon and the materials in which it occurs are the subject of intense study [9].

1.16. Objectives

The objectives of the present work are:

- To crystallize pure ADP and to study the influence of the additives such as L-Ascorbic , DL-Malic and Succinic acid
- To study the crystal structure by powdered X-ray diffraction analysis and FTIR.
- To study the optical and thermal property using UV, DSC/TGA and NLO property from the grown crystals.

CHAPTER II

REVIEW OF LITERATURE

2.1. Introduction

Nonlinear optical (NLO) materials have recently created much attention because of their potential applications in emerging optoelectronic technologies. Potassium dihydrogen phosphate family crystals (KDP, DKDP and ADP) are among the materials most widely used in nonlinear optics, optoelectronics and photonics. Such crystals possess a unique set of properties, including wide transparency range, high laser damage threshold, and can be grown large-sized. This chapter deals with the literature review on article related to ADP (Ammonium Dihydrogen Phosphate) and additives to improve its NLO properties.

2.2. Review on ADP crystals and their dopants

J. Thirupathy 2021 [10] has investigated several applications such as Q-switching, electro-optical and Second Harmonic Generation in nonlinear optics. A good-quality single crystal of ADP was grown using Sankaranarayanan –Ramasamy (SR) method for the dimension of 120 mm in length and 12 mm in diameter. The grown ADP crystal was used for the diverse characterization like FTIR spectral study, Vickers microhardness, Second Harmonic Generation, photoluminescence and chemical eching analysis was used to study the thermal diffusivity of the sample. Thermal transport properties of the crystal are required for all types of heat transfer incidences and furthermore used in seversl applications like acousto-optical, Nd:YAD, and Nd:YLF lasers.

R. Ananda Kumari 2020 [11] has observed the growth of ADP crystals doped with L-Arginine and L-Alanine aminoacids grown from an aqueous solution by slow evaporation technique at constant temperature. The crystalline nature of the grown crystals was confirmed using Powder X-Ray Diffraction technique. The vibrational frequencies of the grown crystals were identified using Fourier Transform Infrared spectroscopy spectral analysis. Optical absorption study has shown a good transparency in the entire visible region was observed with the lower cutoff wavelength of 308 nm and 318 nm for the L-Alanine & L-Arginine doped crystals respectively. The transmission data was for the evalution of optical band gap of

L-Alanine and L-Arginine doped ADP crystals and was found to be 5.023 eV. Second harmonic generation (SHG) studies were performed by the Classical Kurtz powder technique using a Nd: YAG laser operating at 1064 nm. The Second Harmonic Generation efficiency of doped ADP was found to be higher compared to pure ADP crystals.

M. Dhanalakshmi *et al.*, 2020 [12] have observed the growth of single crystals of Fe (II) and Fe (III) (1 mole %) doped ADP crystals. The crystals were grown using slow evaporation method. The grown crystals were characterized by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Ultraviolet-Visible Diffuse Reflectance Spectroscopy. Fourier Transform Infrared Spectroscopy indicates that the percentage of transmittance was lower in case of Fe (III). From the results of UV – visible spectra, it was confirmed that metallic dopants always decreased the transmittance values. Powdered XRD has shown that all have exhibited tetragonal lattice. Thermal studies have shown the information that doped ADP increased the decomposition rate. The second order non-linear property doped ADP brought out that they have good potential for Non-Linear Optic application.

D. Kanimozhi *et al.*, 2019 [13] have reported the growth of potassium dihydrogen phosphate (KDP) single crystal doped with three organic dyes like Alizarin, Congo red and Evans blue using slow evaporation technique. The cell parameters of the pure and doped KDP crystals were found using powder x-ray diffraction. The optical behavior of the pure and doped KDP crystals was analyzed through the UV–Visible absorption spectrum. The functional group analysis of the grown crystals was done using FT-IR spectral study. The emission characteristics of the pure and doped KDP were found using photoluminescence study which resulted in multicolored emission spectra. The second harmonic generation of the pure and doped KDP crystals has shown better frequency conversion property of the crystals. The laser damage threshold (LDT) study was done for all the grown crystals and the results were compared. The growth pattern of the pure doped KDP crystals was examined using etching analysis. The mechanical stability of the grown crystals was determined using Vicker’s microhardness study. The dielectric property of pure and dye doped KDP crystals were carried out at room temperature for different frequencies.

Mohd. Shkir *et al.*, 2020 [14] have investigated the growth of Zinc (tris) thiourea sulphate (ZTS) crystals has been successfully done through slow evaporation technique in presence of L-Ascorbic acid (LAA). The deviation in lattice parameters and shift in peaks position indicates the interaction of LAA with ZTS. Crystalline perfection of grown crystals was judged by High-resolution X-ray diffraction (HRXRD) study and founded that the crystalline perfection of ZTS in presence of 10 wt% LAA was enhanced compared to others. The low optical absorbance and high band gap confirmed its application in optoelectronic devices. A burly blue emission band at 460 nm was observed in Photoluminescence spectra of ZTS crystals grown in presence of LAA when excited at 310 and 358 nm both. However, when these specimens were excited at 385 nm this blue emission band was observed at 470 nm. The remarkable enhancement of blue band emission intensity was noted which may be attributed due to presence of defects (color centers). Further, the dielectric measurement was done and shown the dielectric constant has been improved due to presence of dye. The enhanced optical band gap, photoluminescence intensity and dielectric constant suggested that the LAAZTS single crystals were suitable for electro-optic device applications.

B. R. Thejashwini *et al.*, 2020 [15] have investigated the growth of ammonium dihydrogen phosphate, $NH_4H_2PO_4$ (ADP) single crystals by slow evaporation method. They have correlated the effect of defects present in single crystals with dielectric and other related properties. The phase purity of synthesized ADP crystals was studied by powder X-ray diffraction technique, on finely ground seed crystals. The seed crystals of appropriate size were used for growth of large crystals and also used for dielectric measurements. Two single crystals with different concentrations of defects were used for the investigation of dielectric property at room temperature. The obtained dielectric data were discussed along with their representation in modulus and impedance formalism to understand about the dielectric properties of these crystals. Overall, the low frequency Maxwell–Wagner interfacial polarization was founded to increase due to the presence of defects in ADP single crystals.

Md. Ashiqur Rahman *et al.*, 2019 [16] have reported the growth of ADP single crystal using saturated solution at room temperature by slow evaporation technique, likewise KCl (0.10%M, 0.15%M) doped ADP single crystal also grown. The grown crystals were given for different characterizations like UV- visible spectra and TGA. UV- visible spectra shown that KCl (0.10%M) doped crystal enhance the transmittance above 75% from visible to infrared region but in pure ADP and KCl (0.15%) doped crystal has shown low transmittance due more molecules in the crystal. TGA analysis shown there were no weight loss for pure ADP until 194.02°C, KCl (0.10%M) doped until reaches 184.55°C, KCl (0.15%M) doped until reaches 169.96°C. It was proved that there was no insertion of water in the crystal lattice.

T. Ravichandran *et al.*, 2019 [17] have investigated the growth of ADP crystal in presence amino acids of sarcosine was grown using slow evaporation technique. FT-IR revealed the presence of stronger peak ranges from 1264 cm^{-1} to 1050 cm^{-1} for the NH stretching. UV- Visible spectral analysis indicates the crystal has high transmittance, therefore it exhibited non-linear application. The single crystal X-ray diffraction studies confirmed the tetragonal structure with the space group of I-42d. The crystalline size was calculated as 76.85nm. EDAX confirmed the presence of carbon, oxygen, nitrogen, phosphorus in the grown crystal. The SHG was observed using a Q- switched Nd:YAG laser and its efficiency were found to be better than ADP.

Sasikala Vadivel *et al.*, 2019 [18] have reported the crystal growth of three carboxylic acids - fumaric acid, glutamic acid and succinic acid which were mixed with KDP and ADP for the grow single crystals using slow evaporation method. These transparent crystals were harvested in a period of one month. This grown crystal has shown the relatively sharp XRD reflection which was due to the high crystallinity. FTIR results confirmed that all the crystals have COO^- and P-O vibrations, which was further an evidence for the formation of crystals using carboxylic acids and phosphates. UV –visible spectral studies shown that wide transparency in full visible region indicated that these materials can be used for NLO applications. The more number of weak interaction of fumaric acid with KDP and ADP have increased the thermal stability of FKDP and FADP compare to other carboxylic acids. These grown crystals with high nonlinear response were excellent for SHG device applications. The high SHG efficiency and large band gap properties of crystals have been more useful in NLO and mid-infrared lasers generation.

Fabrício Mendes Souzaa 2017 [19] has investigated the growth of ADP, KDP and KADP crystals by using slow solvent evaporation technique. Impedance spectroscopy was performed to examine the electrical conductivity on KH_2PO_4 (KDP), (NH_4) H2PO4 (ADP) and K_{1-X} $(NH4)_XH_2PO_4$ (x = 0.076, 0.118, 0.357, 0.857, 0.942) crystals with increasing temperature. Z view simulation software was used to theoretically fit electrical conductivity results as a function of frequency (1-106 Hz) and temperature (20-160 ºC) with equivalent circuits. These dielectric-type materials became ionic conductors upon heating. Proton jumps in hydrogen bonds, heavier ions migration (K+ and NH4 +), and rotation and reorientation of ammonium groups contributed to electrical conduction. This conduction behavior followed the Arrhenius equation with which the activation energies were determined at different temperature ranges. For ADP-rich ($x > 0.8$) and pure ADP crystals the conductivities were higher than those for KDP-rich ($x < 0.2$) and pure KDP. Lattice defects may have reduced the electrical conductivities in crystals with intermediate x composition. Complex permittivity ac and complex conductivity ac were also obtained for these crystals.

A.P. Kochuparampil *et al.*, 2017 [20] have investigated the crystal growth of ADP crystals doped with the chalcogenide compound cobalt sulphide (CoS) was doped and the crystals were grown by slow solvent evaporation method. To increase the solubility of CoS in water, its nanoparticles were synthesized by wet chemical technique using ethylene diamine as the capping agent followed by microwave irradiation. The powder XRD pattern has shown the single phase nature of doped crystals. The FTIR spectra confirmed the presence of various functional groups and EDAX gave information about the presence of Co and S elements. The thermo-gram of CoS-doped ADP, the weight loss of 5% was obtained up to 242 ˚C with very slow decomposition. The EPR spectrum confirmed the presence of cobalt and the successful doping of CoS in ADP.

V. Ganesh *et al.*, 2016 [21] have reported the bulk size crystal growth of ADP with different concentrations doping of cobalt (Co^{2+}) have been done by low cost slow evaporation technique at ambient conditions. The solubility measurement was carried out on pure and doped crystal and founded that the solubility was decreased with doping concentrations. The crystallographic structure and lattice parameters of pure and Co^{+2} doped ADP crystals were determined from powder X-ray diffraction analysis. FTIR gave a small shift in main peaks which indicated the effect of metal ion doped on the phosphate and ammonium group. The SEM analysis has shown that the pure crystals contained many growth layers. The main PL band at 330 nm revealed the yield capacity of the material and it was increased with doping concentration, which was a desired property for an optical material for UV light emission. All the studied parameters have show that the properties of ADP have enhanced due to Co^{2+} metal ion doping and it may be suitable for optoelectronic applications.

Kavya. H et *al.*, 2016 [22] have observed the growth and characterization of ADP crystals doped with KBr, KI, $MgCl_2$, LiCl and pure. The result of doped ADP was compared with the results of pure ADP crystals. The crystals have grown using slow evaporation method. Powdered XRD and FTIR spectral analysis confirmed the fact that the lattice sites of ADP crystals were slightly distorted due to the doping of alkali and alkaline metal ions and it retain its original structure. The presence of various groups was confirmed by FTIR analysis. The UV- Visible NIR transparent spectrum has shown that the wide transparency window without any absorption made potential candidate of NLO studies.

Yafei Lian *et al.*, 2016 [24] have reported the growth of ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ADP) crystals by using the temperature reduction method. These grown crystals was used as second, third and fourth harmonic generation material. They described the growth character of ADP and the differences between the growth solubility and structures of KDP and ADP crystal were discussed in details. Ex situ AFM was applied to explore the growth morphology of ADP crystal at different supersaturation. A series of ADP crystals were grown and the transmission spectra of ADP crystal in whole visible region were measured. Laser induced damage threshold (LDT) was measured, which was higher than the average value of LDT of KDP and 70% deuterated DKDP crystal.

Mohd Anis *et al.*, 2015 [25] have studied the growth of ADP crystals doped with sodium metasilicate (SMS) which was grown by slow evaporation solution technique. The unit cell parameters of grown crystal were determined by means of single crystal X-ray diffraction technique. The qualitative analysis of SMS doped ADP crystal was carried out using energy dispersive X-ray and Fourier transform infrared analysis. The increased optical transparency of doped ADP crystal was ascertained in the range of 200–900 nm using UV-visible spectral analysis. The vital optical constants were evaluated using the transmittance data to explore various optical device applications of crystal. The assertive influence of SMS on mechanical and dielectric behavior of ADP crystal was investigated by means of Vickers microhardness analysis and dielectric studies, respectively. The enhancement in second harmonic generation (SHG) efficiency of SMS doped ADP crystal with reference to potassium dihydrogen phosphate (KDP) and ADP was confirmed from Kurtz–Perry SHG test. The Kerr lensing nonlinearity in SMS doped ADP crystal was identified by means of *Z*-scan analysis and the cubic susceptibility (χ3) was founded to be 1.55×10–4 esu, which vitalizes its application for laser stabilization systems.

P. Rajesh, P. Ramasamy 2015 [26] have reported the growth of ADP crystals doped with 1% mole of glycine using the slow cooling technique. UV-Visible spectra result indicated the addition of glycine increased the transmittance. FT-IR result has shown change in the vibrations between 1600 cm^{-1} and 1100 cm^{-1} in the spectrum of glycine doped ADP indicated the presence of glycine in the lattice of the ADP. HRXRD analysis shown that the larger width of the rocking diffraction curve for ADP + Glycine due to higher inner stress in the crystal matrix with incorporated molecules of glycine. The characteristic of high dielectric constant and low dielectric loss with high frequency for a given sample suggests that the sample possessed enhanced optical quality with lesser defects and this parameter was of vital importance for various nonlinear optical materials and their applications. The improved crystalline perfection leads to the increase in the microhardness. Thermal analysis shown the presence of glycine decreases the decomposition temperature of the ADP single crystals. Piezoelectric study has indicated higher piezoelectric coefficient for the doped crystal. The laser damage threshold of glycine doped ADP crystal was high compared to the pure ADP. The higher crystalline perfection of the grown crystal might be responsible for high laser damage threshold.

R.N. Shaikh *et al.,* 2015 [27] have investigated the growth of ADP crystals doped with L-Cysteine using slow evaporation method. The crystal was transparent in the entire visible region, which shown the optical band gap of L- Cytesine doped ADP was found to be 5.35 eV which was greater than the pure ADP. Dielectric studies shown that the low value of dielectric loss of the grown crystal possessed good quality and lesser number of electrically active defects. The thermal studies, the grown crystals can be exploited to any applications below 208°C. The grown crystal belonged to soft material category was determined using microhardness studies. The SHG efficiency of LC doped ADP was founded to be two times more than KDP.

Shaikh Kalim s/o Shaikh Hanif et *al.*, 2015 [28] have presented the crystal growth of ADP doped with the Lithium Chloride of low (3M%LiCl) and high concentration (9M % LiCl). The dopant results in increased meta stable zone width lead to an enhanced crystal growth rate. High concentration of dopant improved the crystalline quality with better transparency. Diffraction pattern revealed that there was no change in basic structure except for variation in intensity of doping; well defined peaks indicate good quality crystal. FTIR spectra has shown some extra peaks which indicated the presence of dopant in ADP crystals. SHG measurement revealed the second harmonic efficiency, has been improved with low concentration of LiCl dopant in ADP crystals. It seemed that the molecular alignment of the crystal facilitated the nonlinearity in the presence of the dopant. They have measured dielectric constant for 3M% and 9M%LiCl crystals found to be deceased with increased frequency.

Congting Sun, Dongfeng Xue 2014 [29] have investigated the hydrogen bonding nature during ADP crystallization was studied on the basis of anisotropic chemical bonding conditions in ADP crystal combined with in situ IR observation. The variations of hydrogen bonding nature of $\mathrm{NH_4^+}$ and $\mathrm{H_2PO_4^-}$ groups dominated the transformation from the free hydrated ionic state to crystalline state during ADP crystallization. Anisotropic ADP crystal morphology depend on the anisotropic chemical bonding conditions along [100] and [101] directions. ADP crystal morphologies with different clusters could be calculated on the basis of hydrogen bonding conditions and cluster structures at the growth interface. The strategy to identify the chemical bonding nature during crystallization processes of molecular crystals from aqueous solution was provided.

Mohd. Hasmuddin *et al.*, 2014 [30] have reported the growth of single crystals of pure ADP and ADP doped with L-tartaric acid (LTA) C4H6O6 were grown by slow evaporation solution technique (SEST) at ambient conditions. Powder X-ray diffraction (PXRD) analysis confirmed the crystal structure and no additional phase were observed due to doping except a systematic variation in peak intensities. Fourier transform infrared spectral analysis examined the presence of various functional groups in the grown crystals. UV-VIS-NIR spectroscopic analysis determined the changes in optical transparency of pure ADP and crystals due to LTA with different doping concentrations. Second harmonic generation (SHG) efficiency measurement analyzed the enhancement in the nonlinear optical characteristics of the grown crystals. The effect of LTA dopant on crystal morphology, thermal and mechanical properties of ADP, reveals the effect of incorporation of LTA into the lattice of ADP crystals.

Dr.M.Selvapandian and R.Arivuselvi 2014 [31] have reported the growth of potassium dihydrogen phosphate and ammonium dihydrogen phosphate single crystals were grown by using slow evaporation method at ambient temperature water as a solvent. The grown single crystals have been analyzed with Fourier infrared spectrometer, Ultra violet and visible spectrometer, Vickers micro hardness test, dielectric studies, thermo grave metric analyses and differential thermal analysis. The presence of functional groups and modes of vibration of the grown crystals was confirmed by FTIR studies. The cut off wavelength of the grown KDP and ADP single crystals were obtained to be 383 nm and 416 nm. Vickers micro hardness studies recorded that the grown both KDP and ADP belonged to the categories of the soft in nature. The thermal behavior of the materials was analyzed by thermo gravimetric and differential thermal analysis (TGA/DTA). The grown materials were thermally stable up to 192°C and 227°C. The dielectric constant and loss of the materials was low at high frequency with different temperature.

P. Rajesh *et al.*, 2013 [32] have investigated the growth of good quality of ADP–KDP mixed crystal (90:10) was grown by slow cooling method. The size of grown crystal was 80*10*10 mm^3. The mounted seed size was 5*10*10 mm^3 and the crystal was grown along the ‘c’ axis. HRXRD studies have been done in the near and far regions of the seed crystal. The close values of FWHM of both the specimens indicated the quality of the crystal remains nearly the same through out the crystal. 80% of transparency was observed from the UV–vis studies in the entire visible region. Vickers hardness studies indicated the mixed crystal was mechanically more stable compared to the ADP. Higher piezoelectric coefficient was observed in mixed crystals. Dielectric measurements were carried out. From the laser damage threshold studies, it was observed that higher energy was required to damage the mixed crystal and it indicated the laser stability of the mixed crystal was high.

A. Jegatheesan *et al.*, 2012 [33] have observed the growth of single crystals of ammonium dihydrogen phosphate using slow evaporation technique at 30° C. In order to study of ADP, they have carried out X-ray diffractometer study on the crystals using Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation. The grown single crystals have analyzed with FT-IR, TGA measurements. Some novel results of a combined sequential study of growth spirals on the basal surface of the richly polytypic ADP crystals by scanning electron microscopy (SEM) was presented and discussed. In the case of transgranular brittle fracture, crystallites split were identified in the SEM images of ADP crystal. The thermogravimetric curve obtained for ADP, there was no weight loss up to 682°C. This indicated there was no inclusion of water in the crystal lattice, which was used as the solvent for crystallization.

Sunil Chaki *et al.*, 2012 [34] have investigated the growth of Ammonium dihydrogen phosphate (ADP) (NH4H2PO4) single crystals doped with sodium metasilicate (SMS) were grown by gel method. The X-ray diffraction analysis of the grown ADP crystals showed that it possessed tetragonal structure having lattice parameters a = 7.502 °A and c = 7.554 °A. The Fourier transform infrared spectroscopy (FTIR) taken for grown ADP crystal between wave-number 400 to 4000 cm^{-1}, which showed peaks due to vibration and stretching of functional group O-N=P and $–ONO_2$ in 485 to 902 cm-1, P=O and O-H in 1076 to 1544 cm^{-1} and O-H and N-H in 2400 to 3371 cm^{-1} range. The UV-Vis-NIR spectroscopy of ADP crystal showed direct optical bandgap of 4.99eV and indirect optical bandgap of 4.12eV. The optical microscopy was employed to study the surface microstructure showed hillocks on the as grown surfaces arising due to local increased supersaturation. The thermal properties of the as-grown ADP crystals were studied by thermogravimetric analysis (TGA). The thermal activation energy determined from the TGA curve using Broido, Piloyan-Novikova (PN) and Coats Redfern (CR) relations were in good agreement with each other.

K. Vanchinathan *et al.*, 2012 [35] have analyzed the Single crystals of Ce(III)-doped ammonium dihydrogen phosphate (ADP) were grown by conventional slow evaporation technique and Sankaranarayanan–Ramasamy (SR) technique. The reduction in the intensities observed in the powder XRD pattern and slight shifts in vibrational frequencies in FT-IR indicated minor structural variations in the doped material. Diffuse reflectance spectral analysis shows that even the low doping of Ce(III)-decreased the reflectance, heavy doping increased the reflectance (lowering of absorption). SEM and EDS analysis shown indicated that the accommodating capability of the host crystal was limited and only a small quantity of Ce(III) were incorporated into the crystalline matrix. Thermal analysis gave the information about the absence of water of crystallization in the molecular structure indicated by the absence of weight loss around 100°C. The efficient SHG demand specific molecular alignment of the crystal facilitating nonlinearity in the presence of dopant.

P. Rajesh *et al.*, 2010 [36] have reported the growth of ADP crystal by addition of Ni^{2+} ions by slow evaporation techniques. The structural performance was studied high resolution XRD. In UV- Visible analysis has shown high transmittance has shown that grown crystal was a good candidate of electro-optics and NLO applications. TG/DTA indicated that decomposition rate of ADP was increased by 8ºC when it is doped by nickel sulphate. Dielectric constant and dielectric loss were for grown crystals for different frequency and different temperature.

P. Rajesh and P. Ramasamy 2010 [37] have observed the good quality ammonium dihydrogen phosphate single crystals added with 1mol% of L-asparagine monohydrate in the mother solution were grown from solutions by slow evaporation, slow evaporation along with seed rotation and Sankaranarayanan–Ramasamy method with the vision to the improved properties of the crystals. The growth rate of Sankaranarayanan–Ramasamy method grown crystal was four times higher than the slow evaporation grown crystal. The grown crystals were found to be transparent in the entire visible region. Thermal stability was higher for L-asparagine monohydrate-added ammonium dihydrogen phosphate crystals. Higher hardness have been obtained for the Sankaranarayanan–Ramasamy method grown unidirectional crystal. Sankaranarayanan–Ramasamy method grown single crystals have low dielectric loss compared to slow evaporation method grown crystal. The second harmonic efficiency was measured for all the crystals and there was no measurable difference obtained between them. The second harmonic relative efficiency of L-asparagine mono- hydrate doped ADP crystal have higher efficiency when compared to pure ADP.

P. Rajesh *et al.*, 2010 [38] have investigated the growth of ADP crystals doped with cobalt (II) acetate hexahydrate and DL-Malic acid using slow evaporation method. UV-Visible spectra shown good transparency in the entire visible region. Vickers hardness measured at room temperature shown increased hardness of the crystal added with DL-malic acid compared to the pure and cobalt (II) acetate hexahydrate added crystals. Dielectric studies revealed the DL-Malic acid added ADP crystal has low dielectric losses. HRXRD analysis exhibited the good crystalline perfection of the grown crystals. The SHG efficiency of DL-malic acid doped ADP crystal was higher than pure ADP crystals.

Zhong Degae *et al.*, 2010 [39] have grown the ADP crystals using the traditional method and rapid growth technology. The optical homogeneity of ADP crystals was analyzed by laser interferometery and X-ray topography. Laser interferometery indicated the refractive index of the prismatic sector is larger. The concentration of Fe and Cr impurities were tested by a plasma emission spectrometer. It was found that the preferential incorporation of metallic impurities into the prismatic faces resulted in high density of growth bands and inclusions thus reduced the optical homogeneity of the prismatic sector.

S. Meenakshisundaram et *al.*, 2009 [40] have grown ADP crystals doped with low (1 M%) and high (10 M%) concentrations of potassium chloride (KCl) . The results exhibited that dopant at low concentrations enhanced crystal growth rate but in the presence of dopant at high concentration decreased the crystal growth rate. Further, low concentrations of dopant improved the crystalline quality with better transparency. The diffraction patterns gave the information that there was no change in basic structure except for variation in intensity by doping. Slight broadening was observed in FTIR of ADP in the 3500 to 3000 cm^{-1} range in the presence of high [KCl]. SEM studies of pure and doped samples revealed that structure defect centers were formed in ADP crystals by the dopant. Second harmonic generation (SHG) efficiency measurements indicated the nonlinear optical (NLO) property was enhanced appreciably by [KCl] dopant and the SHG was more pronounced at high concentrations. It seemed that the molecular alignment of the crystal facilitates non-linearity in the presence of the dopant.

P.Rajesh, P. Ramasamy 2009 [41] have reported the crystal growth of pure ADP and ADP doped with DL Malic acid. The crystals were grown using slow evaporation method and Sankaranarayanan- Ramasamy method (SR) for the improvement of properties of ADP crystals. The result of single crystal revealed the DL- Malic acid entered into the lattice site. The sharp peaks and low full width at half maxima (FWHM) values confirmed the crystallinity of the growth of crystal is good. The effect of DL- Malic acid on the functional group of the pure ADP crystals was identified using the FTIR analysis. The presence DL-Malic acid appearance to decreases the decomposition temperature. The SHG conversion efficiency of doped crystal was 1.5 times than that of pure ADP. The addiction of 1 mole % of DL-Malic acid in ADP was formulated useful for the growth of high-quality, large size ADP crystal with the faster growth rate.

G. Bhagavannarayana *et al.*, 2008 [42] have investigated the growth of ADP crystals doped with KCl and Oxalic acid (over a concentration range from 1 to 10 mol %), namely KCl and oxalic acid ($C_2H_2O4 \cdot 2H_2O$, Oxa) using a slow evaporation technique. The high-resolution X-ray diffraction (HRXRD) studies used to evaluate crystalline perfection revealed some interesting features on the ability of accommodating the dopants by the crystalline matrix. The relative Second Harmonic Generation (SHG) efficiency measurements revealed both KCl and Oxa dopants enhanced the SHG efficiency. However, at higher concentrations of Oxa, SHG efficiency of ADP was not increased but rather decreased from its undoped condition. This might be due to deterioration in the crystalline perfection observed by HRXRD. Powder XRD and FT-IR spectral analysis confirmed slight distortion of the structure of crystal in the presence of a high concentration of dopants (10 mol %). UV–vis study shown the transparency was not affected much by the dopants. The surface morphology of the as-grown specimens, which was changed with the nature and concentration of dopants, was studied by scanning electron microscopy. Presence of dopants was confirmed by energy-dispersive spectrometry.

N. Joseph John and C. K. Mahadevan, 2008 [43] have reported the growth of Ammonium dihydrogen orthophosphate (ADP) crystal which have considered as the nonlinear optical and dielectric material. They have grown ADP crystal doped with NaCl and pure ADP crystal from aqueous solutions pure and the grown crystal has electrically characterized. Density and atomic absorption spectroscopic measurements indicated the impurity molecules have entered into crystal matrix of ADP. DC and AC electrical measurements were carried out at various temperatures ranging between 40°-150°C along both a- and c-directions. They indicate that NaCl addition leads to nonlinear variation of electrical parameters of ADP single crystals with impurity concentration. Activation energies were also estimated.

Xiue Ren *et al.*, 2008 [44] have confirmed the crystal growth of KDP, ADP and KDP mixed with ADP , KADP using slow evaporation method and it was investigated by both experimental and theoretical methods. The molar concentration of ADP saturated solution is approximately two times that of KDP, which influenced the solution stability and consequently the crystal growth rate. The competitive interaction between NH_4^+ and K^+ ion suffer nucleation process due to increased relative molar ratio of KDP. Due to strong bond strength of K-O bond the growth rate along the c-axis of KDP was faster than ADP. These works gave the extended understanding of growth of ADP, KDP and KADP.

S. Krishnan *et al.*, 2007 [45] have reported the growth of single crystals of ferroelectric succinic acid from aqueous solution by low temperature solution growth technique. The cell parameters and space group are found using powder X-ray diffraction analysis. The presence of the functional groups has estimated qualitatively by FTIR analysis. The UV-Visible spectrum shows the cut-off wavelength at 240 nm. The thermal stability of the crystal was studied by TG/DTA. The dielectric constant of the crystal studied as a function of frequency shows the pyroelectric property.

A. Jayarama and S.M. Dharmaprakash , 2006 [46] have reported growth of single crystals of ammonium dihydrogen phosphate (ADP) mixed with different mole concentrations of thiourea were grown using slow evaporation solution technique at 30.8°C. In order to study the effect of mixing thiourea on the structural characteristics of ADP, X-ray diffraction studies were carried out on the crystals using Shimadzu X-ray diffractometer with Cu Ka radiation. X-ray study revealed the structures of thiourea-mixed ADP were slightly distorted compared to the pure ADP crystal structure. Thiourea-mixed ADP crystals were found to have maximum inclusion, as thiourea concentration was 10 mol%.

B. Zizic *et al.*, 1980 [47] have investigated the growth of Ammonium dihydrogen crystals in presence of manganese (II) slats, permanganate and mixtures of the two. They have determined the concentration and oxidation state of incorporated manganese ions. They have also studied the corresponding effects on the crystal habit, as well as kinetic data for growth of the {100} faces of monocrystal. The crystal was grown by the slow evaporation technique. The solution was treated with AgNO3 to find the presence of chlorine ions in the ADP crystal and again to find the presence of manganese ion in crystal, the solution of the crystals was treated with PbO_2 and HNO_3. The Kinetic energy was explained in terms of adsorption of the Mn^{3+} complex with the solution of $AgNO_3$ mixture for pH = 2.5, (b) manganese(II) in ADP solution and Absorption and reflection spectroscopy were used to test for the oxidation states of the manganese ions aqueous solution incorporated in the crystal. The concentrations of manganese ions in the ADP crystal at pH = 2.5 was estimated from the magnetic susceptibility measurements using Wiedemann law.

CHAPTER III

MATERIALS AND METHODOLOGY

3.1. Introduction

Materials and methodology plays an important role in formation of defect free crystals. Defect free bulk single crystals are needed for electronic industries because of their usage in the field of semiconductor, nonlinear optical (NLO), piezoelectric devices and so on. For practical applications, we need good optical transparency and crystal must also withstand high optical power and must be chemically stable. It is difficult to find a material that meets most of the above requirements, however, amino acid crystals are good candidates for NLO applications. In particular, complexes of amino acids and strong inorganic acids play an important role in SHG applications.

3.2. Solvent Evaporation Method

In this method, an excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and solute. In contrast to cooling method, in which total mass of the system remains constant, in solvent evaporation method, the solution loses particles, which are weakly bound to other components, and therefore, the volume of solution decreases. In almost all the cases, vapour pressure of the solvent above solution is higher than the vapour pressure of solute and therefore, solvent evaporates more rapidly and solution becomes supersaturated. Usually, it is sufficient to allow the vapour formed above the solution to escape freely into an atmosphere. This is the oldest method of crystal growth and technically it is very simple.

3.3. Solution and Solubility

A solution is a homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity and that one which gets dissolved in the solution. A solvent choice is chosen in such a way that it possess certain characteristics.

- a good solubility for the given solute
- a good temperature coefficient of solute solubility

- less viscosity
- less volatility
- less corrosion and non-toxicity
- small vapour pressure
- cost advantage

Solvents commonly used include water, ethanol, methanol, acetone, acetonitrile, haxene etc, Almost 90% of the crystals produced from low temperature solutions are grown by using water as a solvent. For crystal growth, high purity water is needed.

3.4. Chemicals Required

3.4.1. Ammonium Dihydrogen Phosphate

Ammonium Dihydrogen Phosphate (ADP) or Monoammonium Phosphate, $NH_4H_2PO_4$, is formed, when a solution of phosphoric acid is added to ammonia until the solution is distinctly acidic. It crystallizes in tetragonal prisms. ADP is a major ingredient of agricultural fertilizers and some fire extinguishers. It also has significant uses in optics and electronics, preparation of baking powder with sodium bicarbonate in fermentation. It supplies soil with the elements nitrogen and phosphorus in a form which is usable by plants. It is used as cleaning products, household care, construction and building materials.

Physical and chemical properties:

- Molecular Formula- $NH_4H_2PO_4$
- Molar mass-115.03 g/mol
- Appearance - white crystals
- Density-1.80 g/cm^3
- Melting point-190°C
- Solubility in water 40.4g/100ml(25°C)
- Solubility insoluble in acetone
- Acidity (pH)-4.2

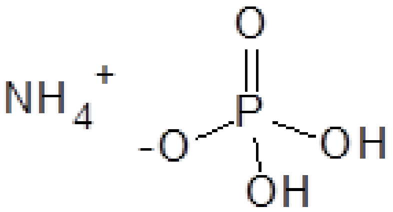

Fig. 3.1. Molecular Structure of ADP

3.4.2. L-Ascorbic Acid

Ascorbic Acid is a natural water-soluble vitamin (Vitamin C). Ascorbic acid is a potent reducing and antioxidant agent that functions in fighting bacterial infections, in detoxifying reactions, and in the formation of collagen in fibrous tissue, teeth, bones, connective tissue, skin, and capillaries. Found in citrus and other fruits and in vegetables, vitamin C cannot be produced or stored by humans and must be obtained in the diet. L-ascorbic acid is a white to very pale yellow crystalline powder with a pleasant sharp acidic taste almost odorless.

Physical and chemical properties:

- Molecular Formula -$C_6H_8O_6$
- Molar mass- 176.12 g/mol
- Appearance - white to very pale yellow crystalline powder
- Density- 1.65 g/cm^3
- Melting point – 190 to 192 °C
- Solubility in water 33 g/100ml
- Solubility insoluble in diethyl ether, chloroform, benzene, petroleum, ether oils and fat.
- Acidity (pH)- 3.5

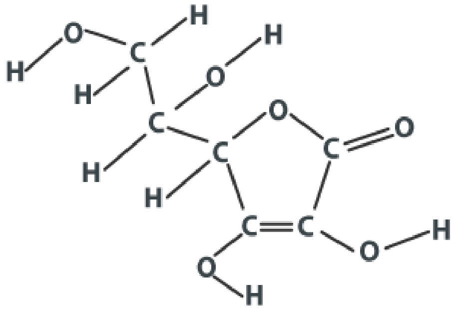

Fig. 3.2. Molecular Structure of L-Ascorbic Acid

3.4.3. DL-Malic Acid

Malic acid is an organic compound with the molecular formula $C_4H_6O_5$. It is a dicarboxylic acid made by all living organisms which contributes to the sour taste of fruits and is used as a food additive. Malic acid has two stereoisomeric forms (L- and D-enantiomers), though only L-isomer exists naturally. The salts and esters of malic acid are known as malates. The malate anion is an intermediate in the citric acid cycle.

Physical and chemical properties:

- Molecular Formula – $CH_2\,COH\,(COOH)_2$
- Molar mass- 134.08 g/mol
- Appearance – colourless
- Density-1.61 g/cm^3
- Melting point- 130°C
- Solubility in water 55.8 g/100 ml
- Acidity (pH)- 3.50

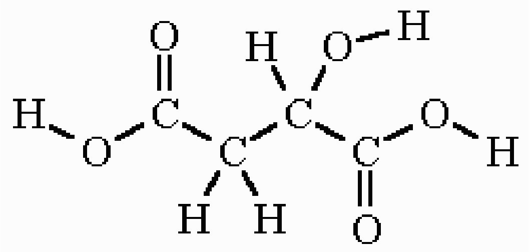

Fig. 3.3. Molecular Structure of DL-Malic Acid

3.4.4. Succinic Acid (SA)

Succinic acid (IUPAC name is butanedioic acid; historically referred to as amber acid) is a dicarboxylic acid having a molecular formula of $C_4H_6O_4$, that can naturally be found in microorganisms, plant, and animal tissues. This organic acid consists of four carbon and two functional carboxyl groups (-COOH) which forms colorless and odorless crystals with a distinctive sour taste. It is also used in foods as a sequestrant, buffer, and a neutralizing agent.

Physical and chemical properties:

- Molecular Formula -$(CH_2)_2$ $(COOH)_2$
- Molar mass-118.09 g/mol
- Appearance - white crystals
- Density-1.56 g/cm^3
- Melting point-185-187°C
- Boiling point- 235°C
- Solubility in water 40.4g/100ml(25°C)
- Solubility insoluble in acetone
- Acidity (pH)-4.2

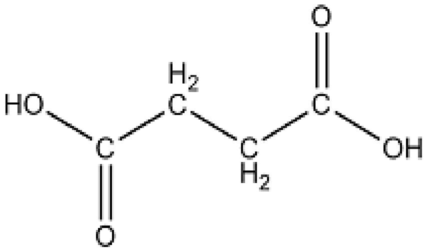

Fig. 3.4. Molecular Structure of Succinic Acid

3.5. Characterization Techniques

Analytical equipment plays an important role in manufacturing and evaluating new products and in protecting consumers and environment. Principle of operation and instrumentation of various techniques used to characterize a pattern are briefly discussed in this chapter. The characterization of a crystal essentially consists of determining composition, structure, defects and study of their optical properties.

The powder samples of the crystals selected for this study were the subject of the following studies:

- Powder X-Ray Diffractometer is used to collect single cells parameters and to confirm the structure of the grown crystals.
- FTIR analysis is used to confirm different functional groups present in the compound.
- UV- Visible spectral analyzer allows to measure optical transmission and absorbance of grown crystals and also to detect transparency.
- Second Harmonic Generation (SHG) test is used to find SHG efficiency of powder of grown crystals.
- Thermal analysis is used to study the thermal stability of growing crystals.

3.6. Powder X-Ray Diffraction

Powder X-ray diffraction (XRD) is a rapid analytical technique mainly, used for phase determination of crystalline materials and can provide information on unit cell size. The analyzing material is finely ground, homogenized, and mean apparent composition is determined.

3.6.1. Fundamental Principles

Max von Laue, in 1912, discovered crystalline substances act as three dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and is directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray), when conditions satisfy Bragg`s Law ($n\lambda=2d\sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning, the sample through a range of 2θ, all possible diffraction directions of the lattice should be attained due to random orientation of the powdered material. Conversion of the diffraction peaks to d spacings allows identification of the mineral, because each mineral has a set of unique d spacings. Typically, this is achieved by comparison of d spacings with standard reference patterns. All diffraction methods are based on generating X-rays in an X-ray tube. These X-rays are directed to the sample and then, capture the diffracted rays. The main factor of any diffraction is the angle between incident ray and diffracted ray. Powder and monocrystalline diffraction differ in instruments outside this range [7].

3.6.2. Instrumentation

An X-ray diffractometer consists of three basic components: an X-ray tube, a sample holder, and an X-ray detector. X-rays are produced in a cathode-ray tube by heating a filament to generate electrons. , by accelerating electrons towards the target by creating an electric potential and bombarding the target material with electrons. When the electrons have enough energy to knock the electrons out of an inner shell of the target material, a characteristic X-ray spectrum is produced. These spectra include several components, the most common being K_α and K_β. K_α is partially composed of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity of $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, and Cr).

Filtering, either by plates or a crystal monochromator is necessary to produce the monochromatic X-rays required for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are close enough in wavelength to use the mean of the two wavelengths. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418 Å. These X-rays are collimated and directed at the sample. As the sample and detector rotate, intensity of the reflected X-rays is recorded. When incident X-ray geometry hits the sample satisfying Bragg equation, constructive interference occurs and an intensity peak occurs. The detector records and processes this X-ray signal and converts it into a count rate, which is then transmitted to a device such as a printer or computer monitor.

The shape of the X-ray diffractometer is such that the sample rotates along the path of the collimated X-ray beam by an angle, while the X-ray detector is mounted on an arm to collect the diffracted and rotated X-rays in an angle of 2θ. The instrument used to maintain angle and rotate the sample is called a goniometer. For typical powder models, data were collected at 2θ from ~5° to 70°, predefined angles during the X-ray scan [46].

3.6.3. Application

X-ray powder diffraction is most widely used to identify unknown crystalline materials (eg, minerals, inorganic compounds). The determination of unidentified solids is essential for studies in geology, environmental science, materials science, engineering, and biology.

- Characterization of crystalline materials
- Identification of fine-grained minerals such as clays and mixed-layer clays that are difficult to identify optically
- Used to determine the unit cell size
- Crystal structure determination

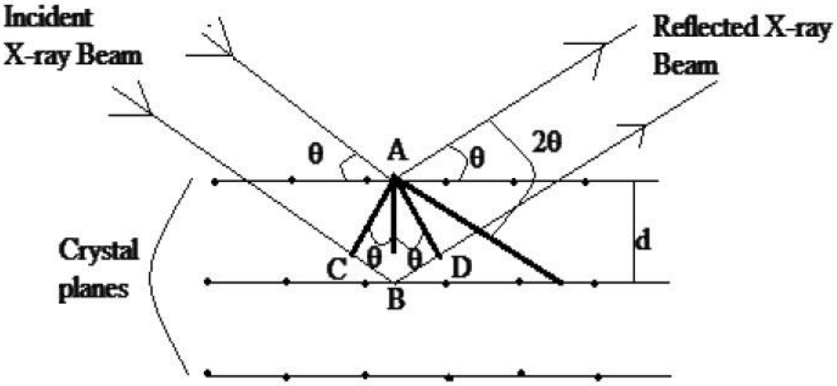

Fig. 3.5. **Powder X-Ray Diffraction**

3.7. Fourier Transform Infrared Spectroscopy

3.7.1 Spectroscopy

Spectroscopy is the study of absorption and emission of light and other radiation by matter. It involves the splitting of light (or more precisely electromagnetic radiation) into its constituent wavelengths (a spectrum), in the same way, prism splits light into rainbow colors. In fact, classical spectroscopy is performed using prisms and photographic plates.

3.7.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material as a function of wavelength. Infrared absorption bands determine molecular composition and structure. When a material is irradiated with infrared radiation, the absorbed IR radiation often excites the molecules to move into higher vibrational states. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the resting and excited vibrational states. The wavelengths absorbed by the sample are characteristic of its molecular structure.

The FTIR spectrometer uses an interferometer to modulate the wavelength of a wideband infrared source. The detector measures the intensity of transmitted or reflected light as a function of its wavelength. The signal received from the detector is an interference program, which must be analyzed by a computer using Fourier transforms to obtain a single beam infrared spectrum. The FTIR spectrum is usually presented as a graph of intensity versus wave number (in cm^{-1}). The wave number is an inverse of wavelength. Intensity can be plotted as a percentage of light transmission or as absorbance at each wave number [47].

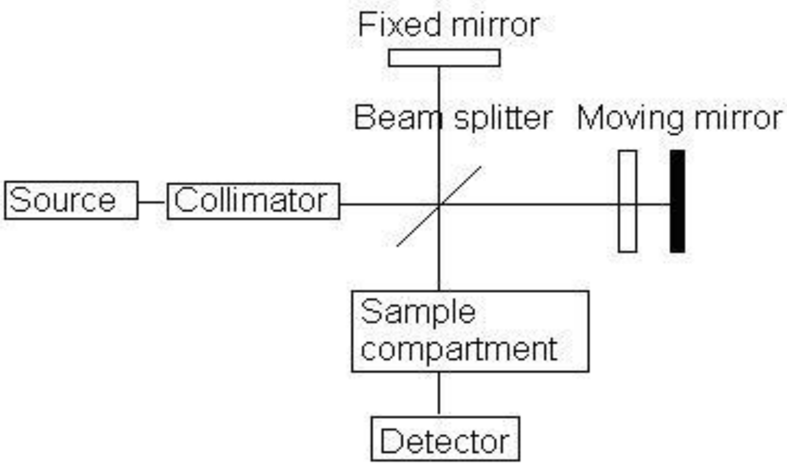

Fig. 3.6. Schematic diagram of a FTIR spectrometer.

3.7.3 Application of FT-IR

FTIR finds application in identifying

- Unknown materials (e.g., films, solids, powders, or liquids)
- Contamination on or in a material (e.g., particles, fibers, powders, or liquids)
- Additives after extraction from a polymer matrix
- Oxidation, decomposition, or uncured monomers in failure analysis investigations

- Deformulation of polymers, rubbers, and other materials through thermogravimetric infra-red (TGA-IR) or gas chromatography infra-red (GC-IR) analysis
- Microanalysis of small sections of materials to identify contaminants
- Monitoring of automotive or smokestack emissions

3.9 Ultraviolet- Visible Spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. It is an analytical method that can measure the sample quantity depending on the amount of light received by the sample.

3.9.1. Principle of UV analyzable spectroscopy

The principle of visible spectroscopy is based on absorption of ultraviolet or visible light by chemical compounds, resulting in the generation of distinct spectra. Spectroscopy is based on an interaction between light and matter. When matter absorbs light, it undergoes excitation and de-excitation, resulting in the generation of a spectrum.

When matter absorbs ultraviolet radiation, the electrons in it are excited. This takes them from the ground state (an energetic state with a relatively small amount of energy associated with it) to the excited state (an energetic state with a relatively large amount of energy associated with it). It is important to note that the difference between energy of the ground state and excited state of an electron is always equal to the amount of ultraviolet or visible radiation, it absorbs.

3.9.2. UV-Visible Spectroscopy and Beer-Lambert Law

Beer Lambert’s law states that, when a monochromatic light beam is incident on a solution containing a monochromatic light absorber, the rate of decrease of light beam along the thickness of solution is proportional to the concentration of the absorbent in solution and is also proportional to the intensity of an incident monochromatic radiation.

According to this law, greater the number of absorbing molecules (capable of absorbing light of a particular wavelength), greater is the degree of radiation absorption.

3.9.3. Application of UV-Visible Spectroscopy

- Quantitative analysis of transition metal ions can be performed using UV-Visible spectroscopy.
- Organic compounds, especially those with a high degree of conjugation, also absorb light in UV or visible region of an electromagnetic spectrum.
- Charge-transfer complexes also give rise to colors, which are often too intense to be used for quantitative measurements.
- Determination of Molecular weight
- Used in detection of functional group
- Detection of impurities

3.10. Thermal Analysis

Thermal analysis may be defined as the measurement of physical and chemical properties of materials as the function of temperature. The thermal analyzer consists of the following components: sensor, furnace, sample and reference holder, and sensor, which heats and cools the sample in the furnace and senses temperature and characteristics of the sample. Temperature controller is used to control furnace temperature. To record and analyze the sensor signals and temperature of a sample, data logger is used. Temperature control, data logging and analysis are all computer controlled. The combination of the furnace and sensor allows for different types of measurement techniques. This computer can be connected to several devices with other types of measurement techniques, allowing simultaneous measurement and analysis [48].

3.10.1. Differential Scanning Calorimetry

The differential scanning calorimeter (DSC) measures the temperature and heat flux associated with heat transitions in materials. Common uses include the investigation, selection, comparison and ultimate performance evaluation of materials in research, quality control, and manufacturing applications. DSC technique include glass transition, cold crystallization, phase change, melting, crystallization, product stability, curing/hardening kinetics, hardness and oxidation stability . DSC is a general term for the following two methods of measurement.

Heat Flux DSC

Technique in which temperature of the sample unit, made up of sample and reference material, is varied in a particular program, and the temperature difference between sample and reference material is measured as a function of the temperature.

Power Compensation DSC

A technique in which the difference in thermal energy applied to a sample and reference material per unit time is measured as a function of temperature to equalize their temperature, while the unit temperature pattern formed by the sample and reference material, which varies within a particular program.

Description of DSC

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid, it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid.

Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle physical changes, such as glass transitions. It is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing.

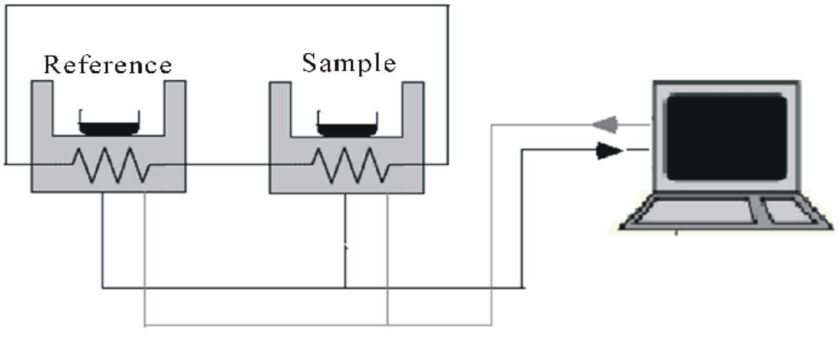

Fig. 3.7. Differential Scanning Calorimetry

Application of DSC

DSC is used to measure changes in enthalpy due to changes in the physical and chemical properties of materials as a function of temperature or time. This method allows you to identify and characterize materials. The differential scanning calorimeter is fast, highly sensitive and easy to use.

3.10.2 Thermogravimetry Analysis (TGA)

Thermogravimetric analysis (TGA) is conducted on an instrument referred to as a thermogravimetric analyser. A thermogravimetric analyser continuously measures mass while the temperature of a sample is changed over time. Mass, temperature, and time are considered base measurements in thermogravimetric analysis while many additional measures may be derived from these three base measurements.

A typical thermogravimetric analyser consists of a precision balance with a sample pan located inside a furnace with a programmable control temperature. The temperature is generally increased at constant rate (or for some applications the temperature is controlled for a constant mass loss). The thermal reaction may occur under a variety of atmospheres includs ambient air, vacuum, inert gas, oxidising/reducing gases, corrosive gases, vapours of liquids or self-generated atmosphere as well as a variety of pressures includs a high vacuum, high pressure, constant pressure, or a controlled pressure. [48].

Application of TGA

TGA can be used to characterize materials through analysis of characteristic decay patterns. It is a particularly useful technique for studying macromolecular materials, including thermoplastics, thermosetting materials, elastomers, composites, plastic films, fibers, coatings, paints, and fuels.

3.10. Non- Linear Optics

Nonlinear optics is completely, a new effect in which light of one wavelength is transformed to light of another wavelength. The creation of light of new wavelength can be understood, only if the nature of the electrons in nonlinear optical crystal is studied.

Electrons in a nonlinear crystal are bound in potential well, which acts like a spring, holding the electrons to lattice point in the crystal (fig.3.7.). If an external force pulls an electron away from its equilibrium position, the spring pulls it back with a force proportional to the displacement. The springs restoring force increases linearly with the electron displacement from its equilibrium position. The electric field in a light wave passing through the crystal exerts a force on the electrons and pulls them away from their equilibrium position. In an ordinary optical material, the electrons oscillate about their equilibrium position at the frequency of this electronic field. According to the fundamental law of physics, an oscillating charge will radiate at its frequency of oscillation, hence these electrons in the crystal "generate" light at the frequency of the original light wave [49].

The nonlinear optical material is different from the linear one in several aspects. The nonlinear optical material can be considered as the one whose electrons are bound by very short springs as shown in fig. 4.7. If the light passing through the material is intense enough, its electric field can pull an electrons so far that they reach the end of their springs. Then, the restoring force is no longer proportional to the displacement and then it becomes nonlinear. The electrons bounce back roughly rather than pulled back smoothly and they oscillate at frequencies other than the driving frequency of the light wave. These electrons radiate at new frequencies, generating new wavelength of light. The exact values of the new wavelengths are determined by the conservation of energy. The energy of the new photons generated by the nonlinear interaction must be equal to the energy of the photon used. Fig. 3.8. Shows the photons involved in second harmonic generation process.

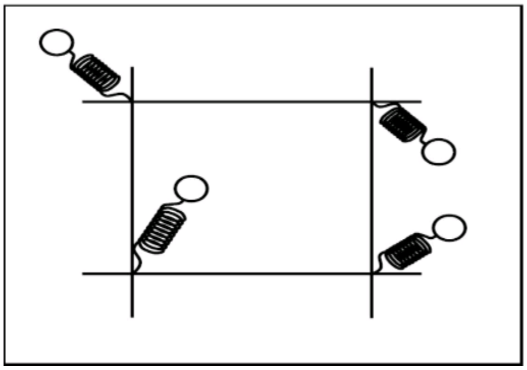

Fig. 3.8. Electrons in a nonlinear crystal are bound in a potential well, holding the electrons to lattice points in a crystal

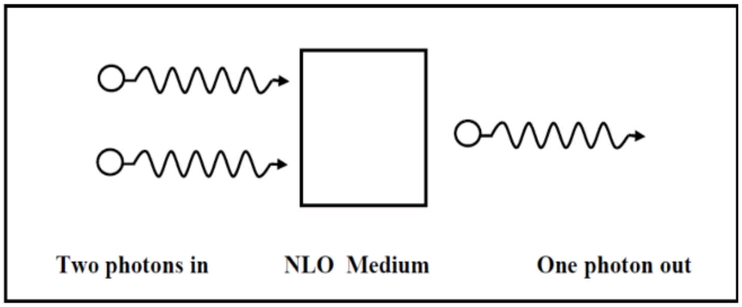

Fig. 3.9. Two photons are welded together to produce a single photon with the energy of both original photons

3.10.1 Second Harmonic Generation

The frequency doubling phenomenon of grown crystal materials has been analyzed using standard Kurtz–Perry powder technique. The single crystals were powdered into micro granules of even size. The prepared samples in the microcapillary tube were photoexcited by the Gaussian beam of Q-switched Nd: YAG laser (1064 nm, 8 ns, 10 Hz, 1.8 mJ pulse). The emission of intense green light at the output window confirmed the NLO behavior of grown crystal compounds. The corresponding output signals of the samples were collected through the photomultiplier tube and the recorded voltages were displayed on the digital oscilloscope [18].

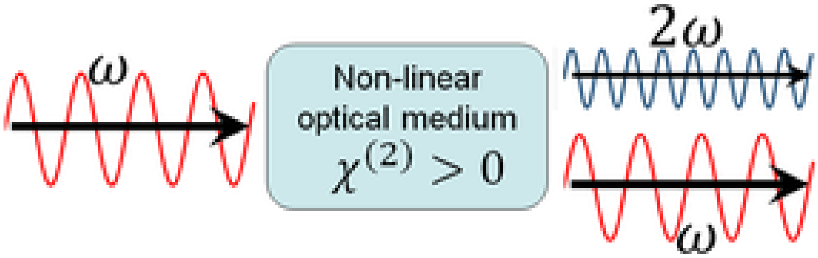

Fig. 3.10. Principle of Second Harmonic Generation

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Introduction

Ammonium dihydrogen phosphate has wide applications such as nonlinear optics, optoelectronics and photonics. Such crystals possess a unique set of properties, including wide transparency range, high laser damage threshold, and can be grown large-sized. This chapter deals about synthesis, results and discussion on the characteristics of the grown crystals.

4.2. Synthesis of the Crystals

4.2.1. Pure ADP

The commercially purchased ADP is used as solute and double distilled water is used as a solvent. For the growth of pure ADP crystal, the ADP is added in the solvent 100 ml of water in terms of 5 grams. The magnetic stirrer is stirred continuously at 40°C and ADP is added till it reaches the point of saturation. After three hours, the saturated homogenous solution is filtered by Whatman filter paper into a beaker. The filtered solution containing beaker is covered with perforated paper, then it is stored and kept at room temperature for slow evaporation. The evaporation of solvent yielded good quality of seed crystal which is shown in Plate No. 4.1. The crystals are grown after 10 days.

4.2.2. ADP doped with L-Ascorbic Acid

Pure chemicals of ADP and L-ascorbic acid with analytical grade are used as solute and double distilled water is used as a solvent. For the growth of ADP crystal doped with L-Ascorbic, ADP and L- Ascorbic acid are taken in the ratio of 1:1 in 100 ml of water. The magnetic stirrer is stirred continuously at 40°C till the solution attains the point of saturation. After three hours, the saturated homogenous solution is filtered by Whatman filter paper into a beaker. The filtered solution containing beaker is covered with perforated paper, then it is stored and kept at room temperature for slow evaporation. The evaporation of solvent yields good quality of seed crystal which is shown in Plate No. 4. 2. The crystals are grown after 15 days.

4.2.3. ADP doped with DL-Malic Acid

The commercially purchased ADP and DL- Malic acid are used as solute and double distilled water is used as a solvent. For the growth of ADP crystal doped with DL-Malic acid, ADP and DL-Malic acid is taken in the ratio of 1:1 in 100 ml of water. The magnetic stirrer is stirred continuously at 40°C, ADP and L- Ascorbic Acid is added till it attains the point of saturation. After three hours, obtained the saturated homogenous solution is filtered by Whatman filter paper into a beaker. The filtered solution containing beaker is covered with perforated paper, then it is stored and kept at room temperature for slow evaporation. The evaporation of solvent yields good quality of seed crystal which is shown in Plate No. 4.3. The crystal grown after 15 days from day the solution keeps for growth.

4.2.4. ADP doped with succinic acid

ADP and succinic acid are used as solute and double distilled water is used as a solvent. For the growth of ADP crystal doped succinic , ADP and succinic acid is taken in the ratio of 1:1 in 100 ml of water. The magnetic stirrer is stirred continuously at 40°C and ADP and succinic acid are added until to attain the point of saturation of the solution. After three hours, obtained the saturated homogenous solution is filtered by Whatman filter paper into a beaker. The filtered solution containing beaker is covered with perforated paper, then it is stored and kept at room temperature for slow evaporation. The evaporation of solvent yields good quality of seed crystal which is shown in Plate No.4.4. The crystals are grown after 10 days.

In the present work, the grown crystals of pure ADP, ADP doped with L-Ascorbic acid, ADP doped with DL-Malic acid and ADP doped with succinic acid are subjected to Powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, thermal, second harmonic generation (SHG) efficiency studies.

Plate 4.1 Photograph of Pure ADP crystal

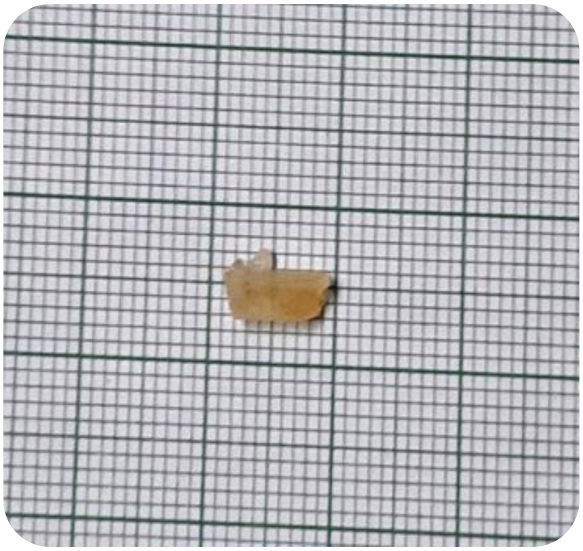

Plate 4. 2. Photograph of ADP doped with L-Ascorbic Acid crystal

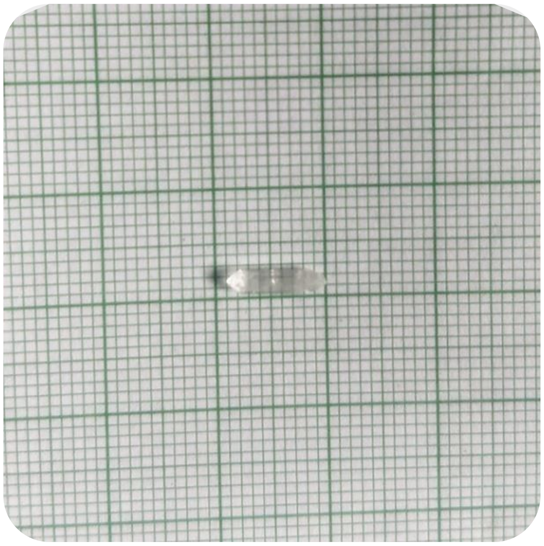

Plate 4.3. Photograph of ADP doped DL-Malic Acid crystal

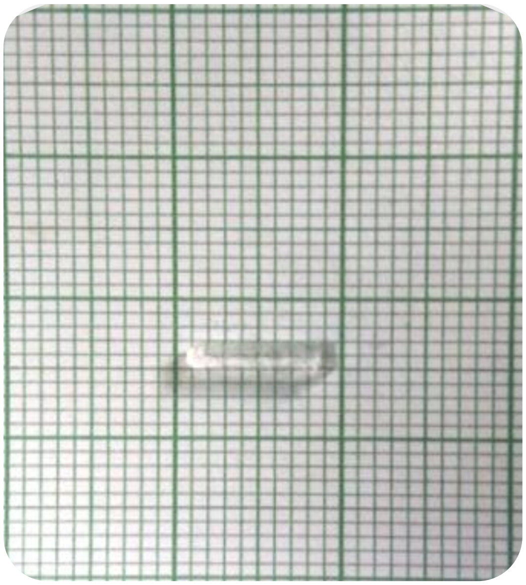

Plate 4.4. Photograph of ADP doped Succinic Acid crystal

4.3. Powder X-ray Diffraction

The powder X-ray powder pattern of grown crystals of pure ADP, ADP doped with L-Ascorbic acid , ADP doped with DL- Malic acid and ADP doped with Succinic acid were obtained by X-Pert Pro PANalytical instrument Goniometer (PW3050/60 Theta/Theta) with Diffractometer system (XPERT-PRO) by CuKα radiation (λ=1.54Ǻ). The powder XRD patterns of the samples are shown in Fig. 4.1. The grown crystals have relatively sharp XRD reflection which is due to the high crystalline nature. The observed prominent peaks of pure ADP are (110), (200), (112), (202), (301) and (312) whereas ADP doped with L-ascorbic is found to have peaks at (002), (011), (021) apart from the ones in pure ADP. These extra peaks correspond to L-ascorbic, which confirms that apart from pure ADP crystals L-ascorbic crystals are also formed. DL- Malic doped ADP crystals are found to have the same peaks as that of pure ADP [41]. This confirms that the original structure of pure ADP is not modified where as the intensities are reduced. The DLM has entered the lattice sites of ADP. In succinic acid added ADP crystal is found to possess the peaks (200) and (301) but they are shifted. New peaks (011), (021) are peaks corresponding to succinic acid [45]. The powder X-ray diffraction confirms that L-ascorbic added ADP forms extra number of new peaks and succinic added ADP forms new peak this indicates that there is a change in the structure of ADP. The result of XRD confirms the mixing of carboxylic acids with phosphate materials to form the complex of crystalline materials.

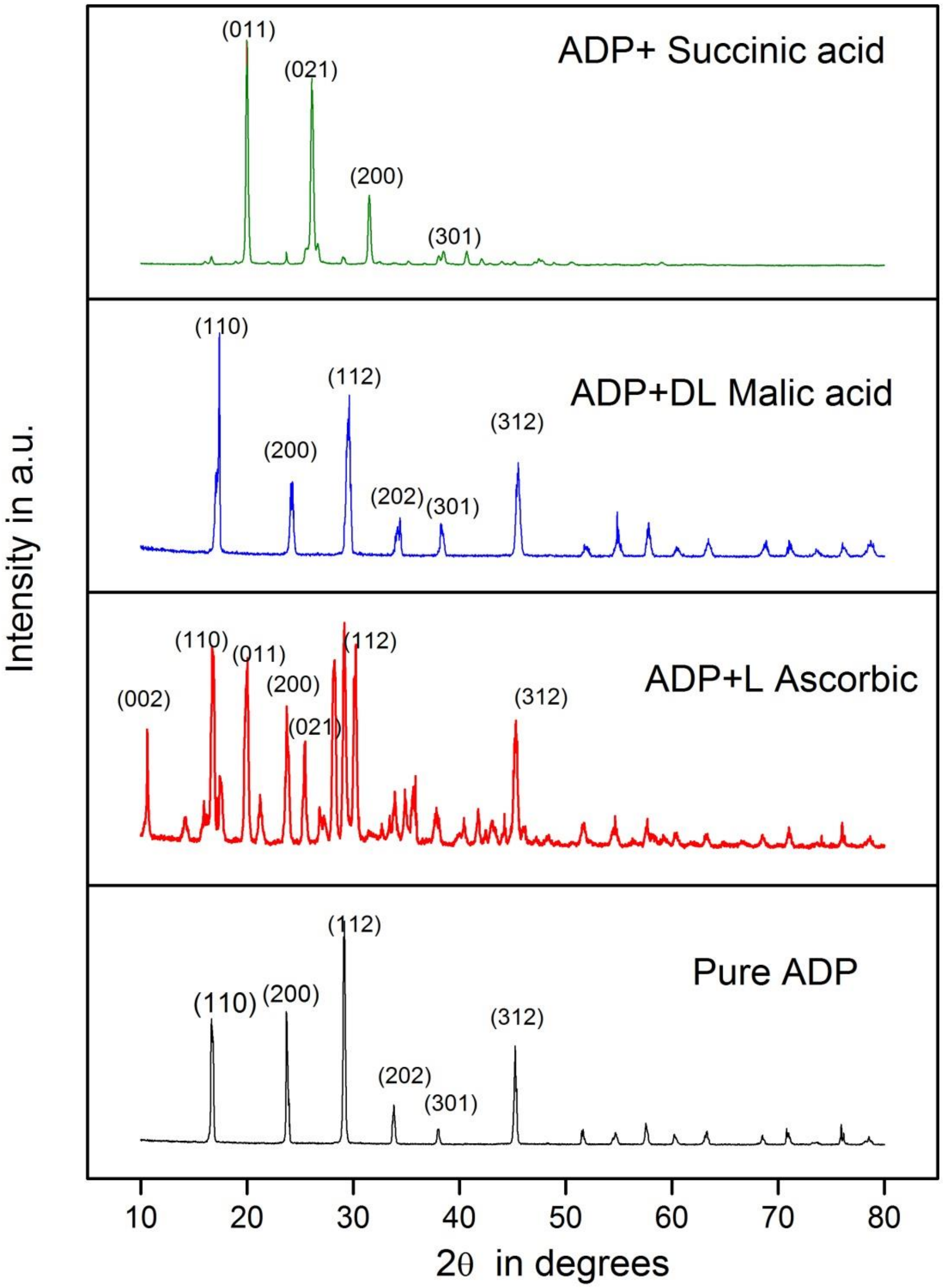

Fig. 4.1. Powder X-Ray Diffraction pattern of the grown crystals

4.4. Fourier Transforms Infrared Spectroscopy

Fourier Transform Infrared Spectra of the grown crystals (Pure ADP, ADP + L-Ascorbic acid, ADP+DL-Malic acid and ADP+ Succinic acid) have been recorded in the region from 400- 4000 cm^{-1} using SHIMADZU Fourier Transform Infrared Spectrophotometer. The FT-IR absorption spectra of the crystals are shown in Fig. 4.2 and spectral assignments of the crystals (Pure ADP, ADP + L-Ascorbic acid, ADP+ DL-Malic acid and ADP+ Succinic acid) given clear information about functional groups present in the compounds. The observed peak wave numbers and their band assignments are presented in Table 4.2. The O-H stretching vibration in hydrates are seen at 3718.76, 3842.20. The O-H stretching vibrations of ADP are seen at 3224.98 cm^{-1}, 3649.32 cm^{-1}, 3402.43 cm^{-1}, 3525.88 cm^{-1}, 3402.43 cm^{-1} and 3309.85 cm^{-1} [47].

Alkanes (CH3, CH_2, CH_3CH_2) presented at 2978.09 cm^{-1} and 2885.51cm^{-1} and C=O band presented at 1689.64 cm^{-1}. The peaks at 1435.18 cm^{-1}, 1404.18 cm^{-1} confirm the presence ammonium ions. P-OH deformations in OH bond are seen in 1388.75 cm^{-1}, 1311.59 cm^{-1}, 1273.02 cm^{-1}, 1396.4 cm^{-1} and 1257.59 cm^{-1}.P=O→H-bonding are seen in 1311.59 cm^{-1}, 1273.02 cm^{-1}, 1219.01 cm^{-1}, 1311.59 cm^{-1}, 1273.02 cm^{-1} , 1219.01 cm^{-1} and 1303.88 cm^{-1}. In plane C-H bending in aryl- phosphoric acid which is seen in only ADP doped L-Ascorbic acid crystals in 1111.00. $H_2PO_4^-$ bonding are seen in 1064.71 cm^{-1}, 1072 cm^{-1}, 1026 cm^{-1}, 1064.71 cm^{-1} and 1080 cm^{-1}. O=P-OH bending are seen in 856.38 cm^{-1}, 864.11 cm^{-1}, 817.82 cm^{-1} and 802 cm^{-1}. OH-P-OH bending in PO_4 vibration are seen in 601.79 cm^{-1} and 601.00 cm^{-1}. The P-O-P is seen at 686.66 cm^{-1} for all the compounds. P^+-O^- deformation in phosphate are seen in 578.64 cm^{-1}, 532.35 cm^{-1}, 486.06 cm^{-1}, 478.35 cm^{-1}, 563.21 cm^{-1} and 462.92 cm^{-1}. FTIR results confirms that ADP + L-Ascorbic acid, ADP+DL-Malic acid and ADP+ Succinic acid crystals have C=O, which is further an evidence for the formation of crystals using carboxylic acids. The presence of peak at 1689.64 cm^{-1} confirm the C=O stretching in the carboxylic acid doped crystal.

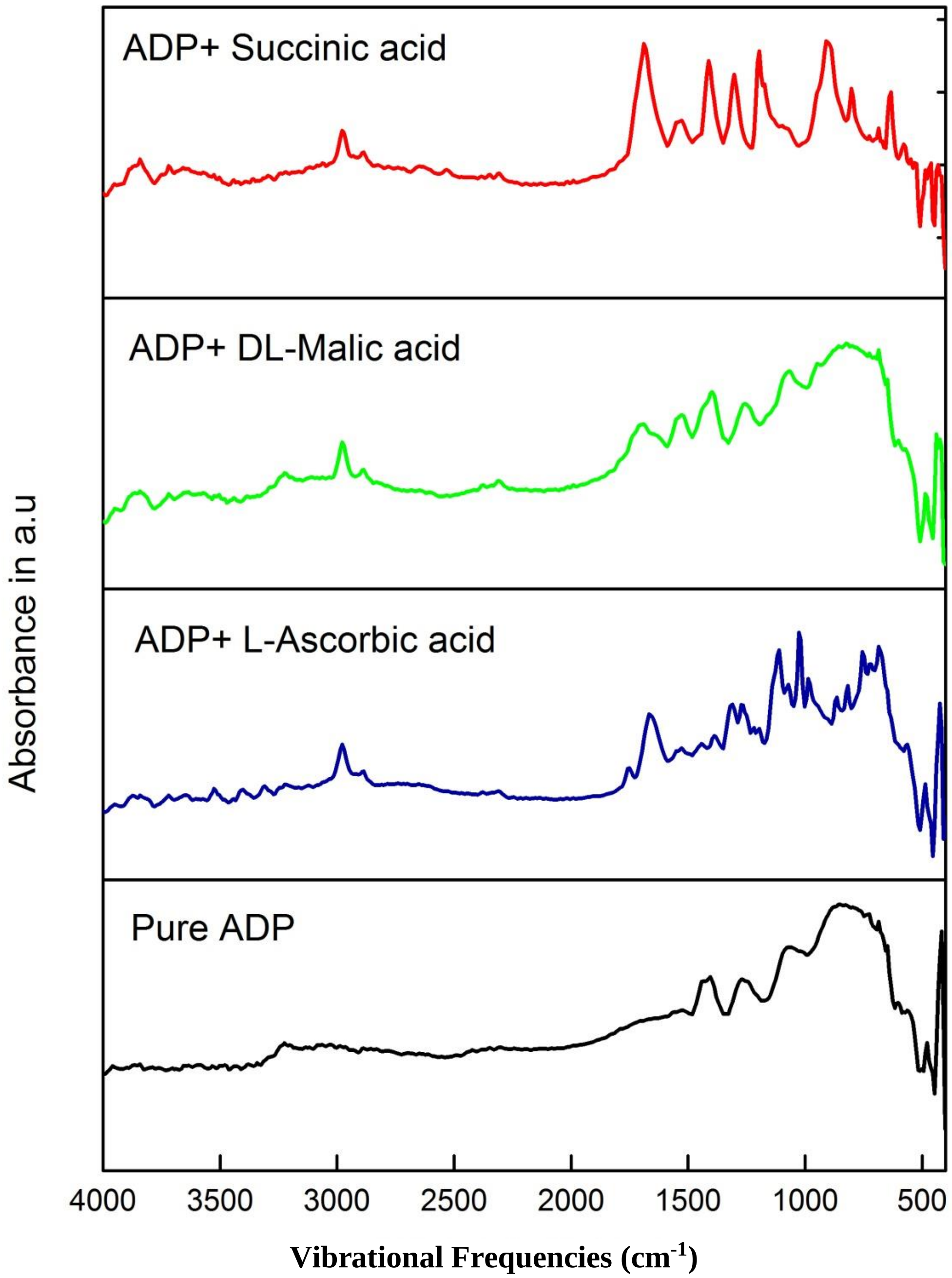

Fig. 4.2. Fourier Transform Infrared Spectroscopy of the grown crystals

Table 4.1. Fourier Transform Infrared Spectroscopy Spectral Assignment for grown crystals

Vibrational frequencies (cm^{-1})				Spectral Assignment
Pure ADP	**ADP + L-Ascorbic acid**	**ADP+ DL-Malic acid**	**ADP+ succinic acid**	
_____	_____	3718.76	3842.20, 3718.76	O-H stretching in hydrates
3224	3649.32, 3525.88, 3402.43, 3309.85	_____	_____	O-H stretching
_____	2978.09	2978.09, 2885.51	2978.09, 2885.51	CH_2 symmetric, asymmetric stretching
_____	1689.64	1689.64	1689.64	C=O (Strong)
	1666.50	_____	_____	Alkenes
_____	1527.62	1527.62	1527.62	OH bending in hydrates
1435.18, 1404.18	_____	_____	_____	NH_4^+ Ammonium ion
_____	1388.75, 1311.59, 1273.02	1396.46, 1257.59	_____	P-OH deformation in OH bond
_____	1311.59, 1273.02, 1219.01	1257.598	1303.88	P=0→H-bonding
_____	1111.00	_____	_____	In plane C-H bending in aryl- phosphoric acid
1064.71	1072, 1026.13	1064.71	1080	$H_2PO_4^-$ bonding
856.39	864.11, 817.82	825.00	802	O=P-OH bending
686.66	686.66	686.66	686.66	P-O-P linkage
601.79	601.00	601.00	601.00	OH-P-OH bending in PO_4 vibration
478.35	563.21, 486.06	486.06	578.64, 532.35, 486.06, 462.92	P^+-O^- deformation in phosphate

4.5. Ultraviolet- Visible Spectral Studies

The UV-Visible spectral analysis of the grown crystals solution are carried out using Biospec Nano Spectrophotometer for Absorbance in the range between 200-800 nm and it was shown in Fig. 4.3. Cutoff wavelength of the grown crystals is observed in the wave length range of 300-365 nm. The wide transparency in the full visible region indicates that these materials can be used for NLO applications. The higher bandgap properties of these materials will be useful in mid-infrared lasers generation the application.

The transmittance percentage of pure ADP shows 92.46 % whereas the transmittance percentage of ADP doped l-ascorbic acid shows 93.32 %, ADP doped DL-Malic acid shows 98.40%, ADP doped succinic acid shows 97.50 % of transmittance. Bandgap energy is found using UV- visible absorbance data using the Tauc plot method and it is found that pure ADP and DL-Malic acid has same bandgap energy and it was reduced a little for L-Ascorbic and Succinic acid added ADP crystal.

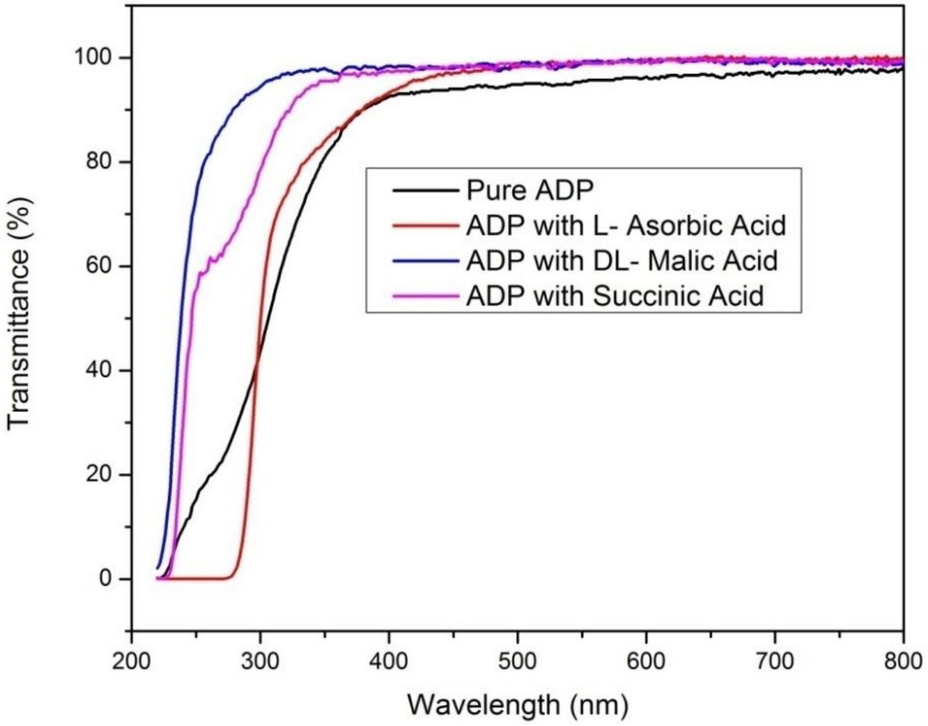

Fig. 4.3. Ultraviolet-Visible transmittance of the grown crystals

Table 4.2. Bandgap Energy of compounds

S.No	**Compounds**	**Bandgap Energy (eV)**
1.	Pure ADP	5.4
2.	ADP doped with L- Ascorbic acid	4.3866
3.	ADP doped with DL-Malic acid	5.3755
4.	ADP doped with Succinic acid	5.4

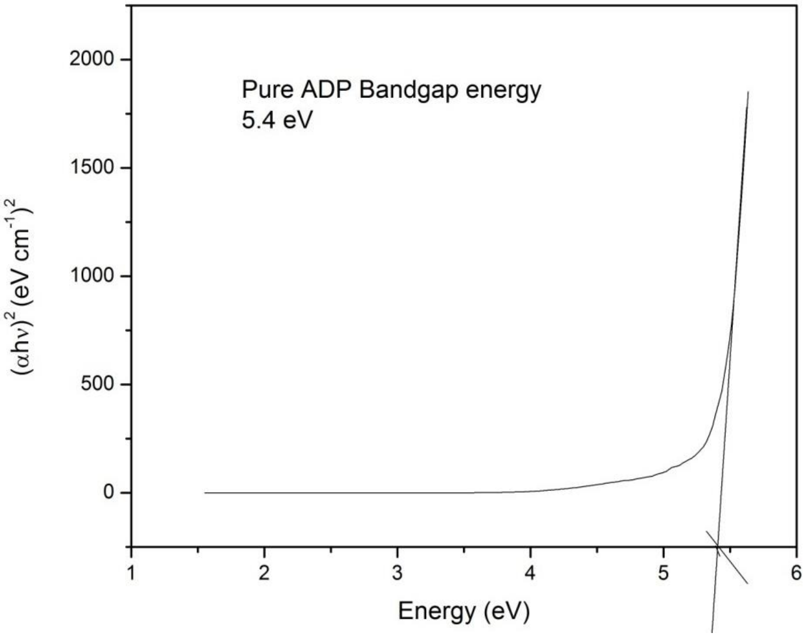

Fig. 4.8. Tauc plot for bandgap energy of Pure ADP crystals

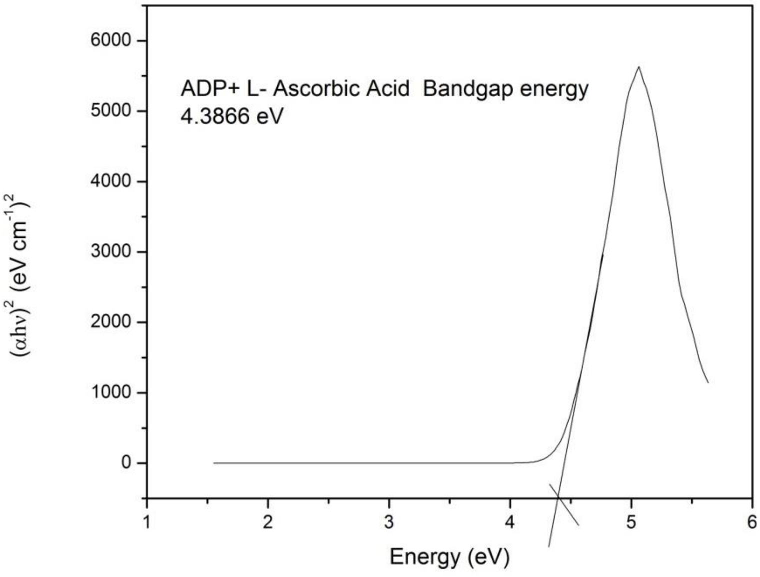

Fig. 4.4. Tauc plot for bandgap energy of ADP doped with L-Ascorbic Acid crystals

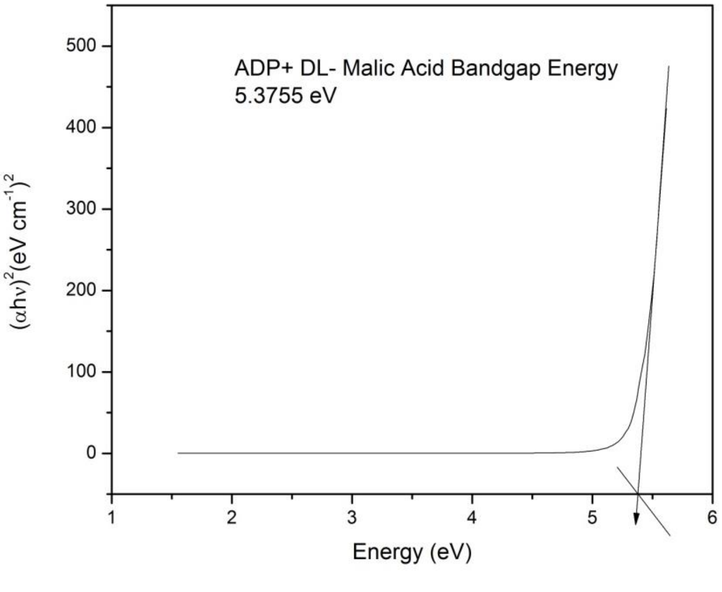

Fig. 4.5. Tauc plot for bandgap energy of ADP doped with DL-Malic Acid crystals

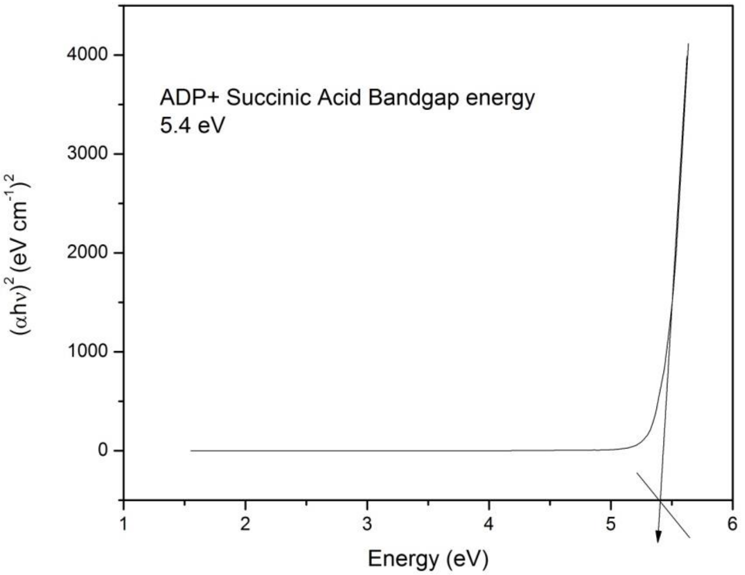

Fig. 4.6. Tauc plot for bandgap energy of ADP doped with Succinic Acid crystals

4.6. Thermal Analysis

The simultaneous DSC/TGA curves for pure ADP and doped ADP systems recorded in nitrogen ambient in the temperature range between 28 and 500°C at a heating rate of 2°C/ min are given in the Fig. 4.7 to 4.10. The absence of water of crystallization in the molecular structure is indicated by the absence of weight loss around 100°C. The thermo gravimetric analysis is performed for pure and ADP crystals doped with Carboxylic acids. All the three carboxylic acid gives decrease in the decomposition point with respect to pure ADP. Significant variations are observed and the presence of decomposition below the melting point ensures that the material is not suitable for application in lasers since the crystals are not able to with stand high temperatures.

DSC curves of pure ADP, L-Ascorbic acid doped ADP, DL- Malic acid doped ADP and succinic acid doped ADP are presented in Fig. 4.7 to 4.10 respectively along with TGA. All the four DSC curves exhibit an endothermic peak at 225.08, 164.18, 207.58 and 215.90°C, respectively. The addition of L-Ascorbic acid has shifted the melting point lower (164.18°C) than the pure ADP melting point (225.08°C). But the addition of DL-Malic acid has shifted the melting point a little bit lower (207.58°C) than the pure ADP melting point (225.08°C) . The addition of Succinic acid has shifted the melting point to lower value (196.79°C) than the pure ADP melting point (225.08°C).

Table 4.3. DSC/TGA results for grown crystals

S.No.	Compounds	Temperature (°C)	Endothermic/ Exothermic	Decomposition Point (°C)
1.	Pure ADP	209.27 223.0	Endothermic	202.15
2.	ADP doped with L- Ascorbic acid	165.66 263.16	Endothermic Exothermic	164.18
3.	ADP doped with DL-Malic acid	207.58 219.53 252.06 349.49	Endothermic Exothermic	207.60
4.	ADP doped with Succinic acid	196.19 229.82 246.29 370.84	Endothermic Exothermic	215.90

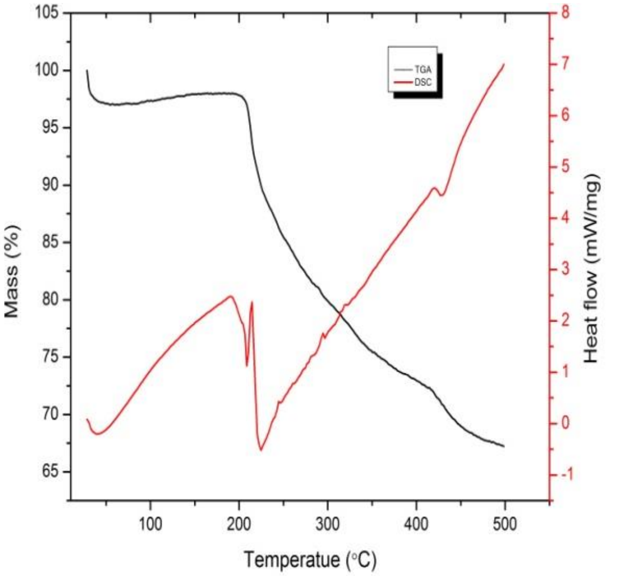

Fig. 4.7.DSC/TGA of pure ADP

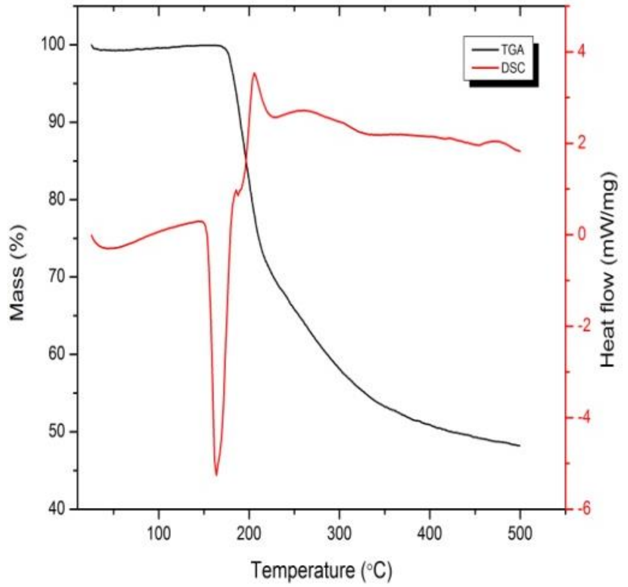

Fig. 4.8.DSC/TGA of ADP doped with L-Ascorbic Acid

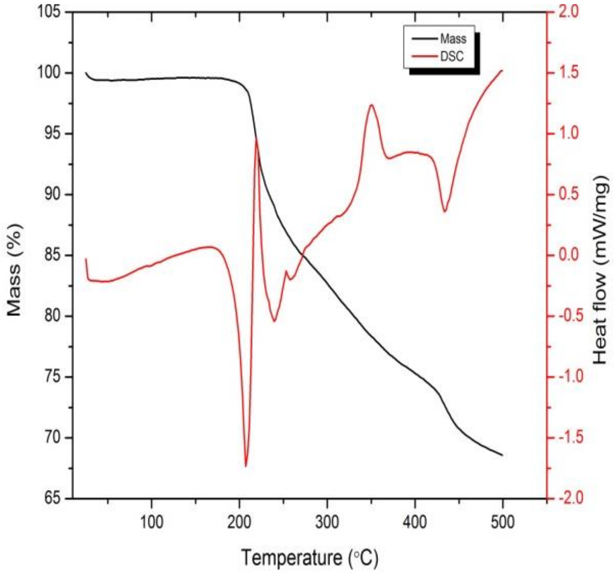

Fig. 4.9.DSC/TGA of ADP doped with DL-Malic acid

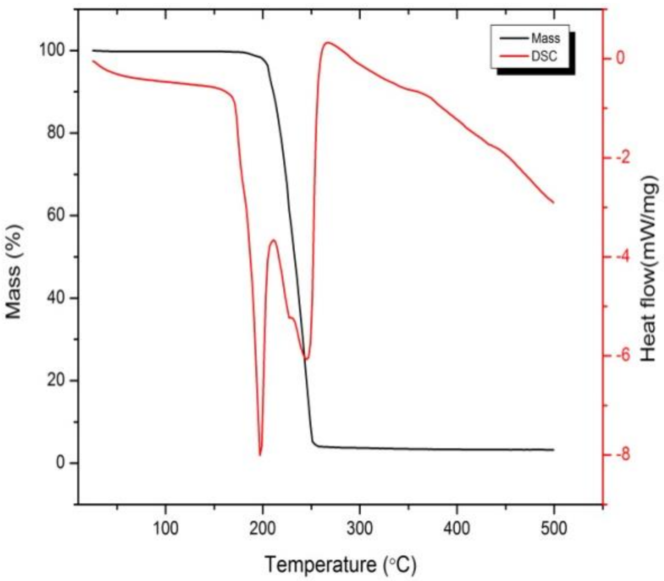

Fig. 4. 10. DSC /TGA Curve of ADP doped with Succinic Acid

4.7. Non- Linear optical studies

The frequency doubling phenomenon of grown crystal materials has been analyzed using the standard Kurtz–Perry powder technique. The single crystals were powdered into micro granules of even size were packed in a sample tube and exposed to Nd:YAG laser with 1064 nm radiation. The generation of second harmonic was confirmed by the emission of green light with a wavelength of 532 nm from the sample. KDP is used as reference material in the present investigation. The output SHG efficiency for pure ADP is found to 21 mV, that of L-Ascorbic added ADP, DL-Malic added ADP and Succinic Acid added ADP are found to respectively 4 mV, 21 mV, 5mV. It is noticed the efficiency is high for pure ADP and it is maintained in DL-Malic acid added ADP; whereas it is reduced to 1.5 times for L-Ascorbic added ADP and 1.7 times for Succinic added ADP. The values are tabulated in Table 4.4.

Table 4.4. Second Harmonic Generation results for grown crystals

S.No	Compound	I_{SHG} (mV)
1.	Pure ADP	21
2.	ADP doped with L-Ascorbic acid	4
3.	ADP doped with DL-Malic acid	21
4.	ADP doped with Succinic acid	5

CHAPTER V

SUMMARY AND CONCLUSION

ADP crystals have efficient optical frequency conversion and are the key elements for the development of laser systems, telecommunication industry, optical information processing, high optical disk data storage, wide range tunable sources of coherent illumination in ultra-violet, visible and infrared spectral ranges. Crystals of L-Ascorbic acid doped ADP, DL-Malic acid doped ADP, Succinic acid doped ADP and pure ADP have been grown using slow evaporation method with the vision to improve the properties of ADP crystals. Distilled water was used as the solvent. Grown crystals are characterized using Powder X-Ray Spectroscopy, UV-Visible spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry/ Thermal Gravimetric Analysis (DSC/ TGA) and SHG studies. The result of XRD confirms the mixing of carboxylic acids with phosphate materials to form the complex of crystalline materials. FTIR confirms that the presence of peak at 1689.64 cm^{-1} confirm the C=O stretching in the carboxylic acid doped crystal. The enhancement in transmittance is noted when the additives are added in pure ADP. Observation in TGA shows the presence of decomposition below the melting point which ensures that the material is not suitable for application in lasers where the crystals are not able to with stand high temperatures. However the coating may be used for thin film applications. All the four DSC curves exhibit an endothermic peak at 225.08, 164.18, 207.58 and 215.90°C, respectively. Melting point of pure ADP is high when compared to other crystals. Second harmonic generation (SHG) efficiency is measured to examine the enhancement in the non-linear optical characteristics of the grown crystals. The efficiency of NLO is enhanced in DL-Malic acid added ADP.

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