Spectroscopic Characterizations of Organic/Inorganic Nanocomposites

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SPECTROSCOPIC CHARACTERIZATIONS OF

ORGANIC/INORGANIC NANOCOMPOSITES

JAYESH R. GOVANI

Materials Science and Engineering

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Dean of the Graduate School
Dedicated
To
My
Beloved
Parents
SPECTROSCOPIC CHARACTERIZATIONS OF
ORGANIC/INORGANIC NANOCOMPOSITES

By

JAYESH R. GOVANI, M.Sc, M.Phil

DISSERTATION
Presented to the Faculty of the Graduate School of
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of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

Materials Science and Engineering
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Abstract

Nonlinear optics (NLO) has wide applications in the fields of telecommunications and information devices and it plays a vital role in the emerging photonics and optoelectronics technologies. Hence, nonlinear optical frequency conversion materials have garnered noteworthy attention and interest with the dawn of plenty of devices utilizing solid state laser sources, because of their significant impact on laser technology, optical communication and optical data storage. Ideal materials for utilization in nonlinear optics must exhibit certain distinct properties such as a large nonlinear coefficient for frequency conversion together with large transparency range, high laser damage threshold, fast optical response time, mechanical stability and chemical inertness as well as architectural flexibility for molecular design and morphology. Generally most inorganic crystals exhibit certain important nonlinear optical properties such as high damage threshold, good transparency, chemical stability and good hardness. On the other hand, organic materials are promising as a substitute for inorganic materials for their use in nonlinear optics and devices because of their adaptability and the possibility of tailoring them for a particular device application. However, they also exhibit certain shortcomings, such as poor mechanical and thermal properties, susceptibility to damage during processing, etc. Organic and inorganic materials possess their own respective drawbacks. Hence, in order to overcome the inherent limitations on the maximum attainable nonlinearity in inorganic materials and the limited success in growing device-grade organic single crystals, a new class of NLO materials i.e. hybrid organic-inorganic, or semiorganic, has evolved.

Potassium dihydrogen phosphate (KDP) is an inorganic material widely known for its assets as a nonlinear optical material. On the other hand, α–amino acids have proven to be perfect candidates for NLO applications, since they contain certain special features like
molecular chirality, weak Vander Waals and hydrogen bonds, absence of strongly conjugated bonds and wide transparency range. Hence, doping KDP crystals with amino acid families has been under extensive investigation in recent times because of constructive improvement of the NLO properties of standard KDP crystals.

In the present study, pure and 0.3 wt%, 0.4 wt%, as well as 0.5 wt% L-arginine doped KDP crystals were grown using solution growth techniques and further subjected to infrared (IR) absorption and Raman studies for confirmation of chemical group functionalization for investigating the incorporation mechanism of the L-arginine organic material into the KDP crystal structure. Infrared spectroscopic analysis suggests that structural changes are occurring for the L-arginine molecule as a result of its interaction with the KPD crystal. Infrared spectroscopic technique confirms the disturbance of the N-H, C-H and C-N bonds of the amino acid, suggesting successful incorporation of L-arginine into the KDP crystals. Raman analysis also reveals modification of the N-H, C-H and C-N bonds of the amino acid, implying successful inclusion of L-arginine into the KDP crystals. With the help of Gaussian software, a prediction of possible incorporation mechanisms of the organic material was obtained from comparison of the simulated infrared and Raman vibrational spectra with the experimental results. Furthermore, we also studied the effect of L-arginine doping on the thermal stability of the grown KDP crystal by employing Thermo gravimetric analysis (TGA). TGA suggests that increasing the level of L-arginine doping speeds the decomposition process and it weakens the KDP crystal, which indicates successful doping of the KDP crystals with L-arginine amino acid.

Urinary stones are one of the oldest and most widely spread diseases in humans, animals and birds. Urolithiasis is a universal problem regardless of geographical, cultural or racial groups and the diagnosis and treatment of calculi stones is extremely expensive. Although significant
knowledge about kidney stones has been acquired, their recurrences demonstrate that this phenomenon is quite complex and cannot be eliminated completely. Possible factors in their formation are heredity, environment, age, sex, urinary infection, diet, and metabolic diseases; however, the precise reasons for the formation of kidney stones are not completely identified to date.

Many remedies have been employed through the ages for the treatment of urinary stones. Recent medicinal measures reflect the modern advances, which are based on surgical removal, percutaneous techniques and extracorporeal shock wave lithotripsy (ESWL). Although these procedures are valuable, they are quite expensive for most people. Furthermore, recurrence of these diseases is awfully frequent with these procedures and the patients have to be subjected to careful follow up for several years. In contrast, in traditional therapeutic systems, most of the remedies were taken from plants and they proved to be helpful. However, the rationale behind their use is not thoroughly established through systematic pharmacological and clinical studies. In this regard, in the present investigation, with a view towards acquiring more insights, we have performed a detailed study of kidney stone formation and growth inhibition based on a traditional medicine approach with herbal extracts.

The intricacy of calculi formation (i.e. nucleation, transformation, and aggregation) in a natural system such as urine is replicated to a certain extent in the present study by using a simplified single diffusion gel growth technique. Crystals were synthesized in a static gel environment without and with the presence of 1% and 2% concentration of Rotula Aquatica Lour (RAL) herbal extracts and further subjected to Raman, infrared absorption, X-ray photoelectron spectroscopy (XPS), and photoluminescence to analyze the effects of RAL on the growth of manganese-based calculi.
Raman spectroscopy clearly provided an indication of the newberyite type of crystal as well as information on the chemical interaction between crystal and inhibitor. It also indicates the presence of organic components due to the RAL plant material. Infrared absorption spectroscopy indicates the presence of a strong reflecting component in the inhibitor as well as the newberyite type of crystal. XPS results indicated the presence of metallic zinc in the crystal with inhibitor. Furthermore, a considerable increase in the intensity of the magnesium and oxygen lines are noticed with the addition of the herbal extract, which suggest that the inhibitor chemical composition includes a substantial quantity of Mg and O. XPS analysis also demonstrates the presence of modified phosphorus oxidation states and suggest that they might make a contribution, too. The photoluminescence spectra of the crystal with inhibitor indicate the presence of chlorophyll, and hence, confirm the presence of Mg.

This study provides evidence of Mg- and Zn- related inhibition of urinary calculi formation with the addition of RAL herbal extract, contributing, from the spectroscopic point of view, to an intricate subject. Our present investigation might serve as an important source of information on this tantalizing and multifaceted problem, which is not yet completely understood.
# Table of Contents

Acknowledgements........................................................................................................... iv

Executive Summary........................................................................................................... vi

Table of Contents............................................................................................................. x

List of Tables...................................................................................................................... xvi

List of Figures.................................................................................................................... xviii

Chapter 1 INTRODUCTION

1.1 Research Motivation........................................................................................................ 1

   1.1.1 L-arginine doped Potassium Dihydrogen Phosphate (KDP) crystals................................. 1

   1.1.2 Kidney stone formation and its inhibition by herbal extracts........................................... 5

1.2 Dissertation Outline......................................................................................................... 7

Chapter 2 THEORETICAL BACKGROUND

2.1 Introduction to nonlinear optical materials........................................................................ 10

   2.1.1 Highlights of nonlinear optics.......................................................................................... 10

   2.1.2 Linear versus nonlinear optics....................................................................................... 11

   2.1.3 Origin of optical nonlinearity.......................................................................................... 12

   2.1.4 Brief history.................................................................................................................... 17

   2.1.5 Second harmonic generation and frequency mixing...................................................... 18

   2.1.6 Materials point of view.................................................................................................. 20
2.1.6.1 Importance of laser damage threshold value ........................................... 22

2.1.7. Inorganic nonlinear optical materials ............................................................ 23

2.1.7.1. Potassium Dihydrogen Phosphate (KDP) crystals

   as NLO material .................................................................................................. 26

2.1.8. Organic nonlinear optical materials .............................................................. 27

2.1.8.1. L-arginine organic nonlinear optical material ........................................ 28

2.1.9. Hybrid organic-inorganic nonlinear optical materials ............................... 31

2.2. Introduction to renal calculi ........................................................................... 34

2.2.1. Past, present and future of urolithiasis ....................................................... 36

2.2.3. Composition of urinary calculi ................................................................... 40

2.2.3.1. Struvite or infection stones .................................................................... 40

2.2.4. Importance of traditional approach to nephrolithiasis .............................. 44

2.2.4.1. ‘Ayurveda’- Indian traditional curative system in urolithiasis ................. 44

2.2.4.2. Rotula Aquatica Lour ............................................................................ 45

Chapter 3 EXPERIMENTAL TECHNIQUES

3.1. Crystal Growth ............................................................................................... 47

3.1.1 Comparison of Different Growth Techniques ............................................. 50

3.2 Aqueous Solution Growth Techniques ............................................................ 51

3.2.1 Crystal Growth by Slow Evaporation of the Solvent ................................. 52

3.2.2 Crystal Growth by Slow Cooling of the Solvent ........................................ 53

3.2.3 Sample Preparation for L-arginine Doped KDP Crystals ......................... 53
3.2.3.1 Preparation of seed crystals .............................................................54

3.2.3.2 Preparation of larger sizes of pure and L-arginine doped KDP single crystals .............................................................54

3.3 Gel Growth Technique ...................................................................57

3.3.1 Brief History of Gel Growth .........................................................57

3.3.2 Gelling Mechanism .....................................................................58

3.3.3 Structure of Silica Hydrogel ...........................................................59

3.3.4 Gel Growth Methods ....................................................................61

3.3.4.1 Crystal Growth by Reaction ......................................................61

3.3.4.2 Chemical Reduction Method ......................................................63

3.3.4.3 Complex-Decomplexion Method ...............................................64

3.3.4.4 Solubility Reduction Method ......................................................64

3.3.4.5 Electrolytic Method .................................................................64

3.3.5 Simple Model for In Vitro Study .....................................................66

3.3.6 Sample Preparation for pure and Rotula Aquatica Lour (RAL) incorporated struvite crystals .........................................................67

3.4 Thermogravimetry .........................................................................68

3.5 Fourier Transform Infrared (FT-IR) Spectroscopy .........................69

3.6 Raman Spectroscopy .......................................................................71

3.6.1 The theory of Raman spectroscopy .............................................72

3.7 Comparison of Infrared Absorption and Raman Spectroscopy ........76
3.8 Bruker IFS66v FT-IR Spectrometer

3.9 An alpha 300 WITec confocal Raman Spectrometer

3.10 X-ray Photon Spectroscopy (XPS)

3.10.1 Physics of X-Ray Photoelectron Spectroscopy

3.10.2 XPS Instrumentation

3.10.3 Applications of XPS

3.10.4 Limitations of XPS Characterization

3.10.4.1 Quantitative Precision Limit

3.10.4.2 Detection Limits

3.10.4.3 Analysis area limits

3.10.4.4 Sample size limits

3.10.4.5 Degradation during analysis

3.10.5 Materials routinely analyzed by XPS

3.11 Photoluminescence Spectroscopy

3.11.1 Instrumentation for Photoluminescence

3.11.2 Applications of Photoluminescence

3.11.2.1 Band Gap Determination

3.11.2.2 Impurity Levels and Defect Detection

3.11.2.3 Recombination Mechanisms

3.11.2.4 Quality of Materials

3.11.3 Special Features of Photoluminescence Spectroscopy

3.11.4 Pros of Photoluminescence

3.11.5 Cons of Photoluminescence
### Chapter 3

3.11.6 Confocal Photoluminescence Spectroscopy

3.11.7 Importance of Photoluminescence

3.12 Horiba-Jobin Yvon INDURAM Spectrometer

### Chapter 4

**SPECTROSCOPIC CHARACTERIZATION OF L-ARGININE DOPED POTASSIUM DIHYDROGEN PHOSPHATE CRYSTALS**

4.1 FT-IR Spectroscopic Investigation

4.2 Raman Spectroscopic Characterizations

4.3 Thermo Gravimetric Analysis (T.G.A.)

### Chapter 5

**SPECTROSCOPIC STUDY OF URINARY CALCULI INHIBITION BY HERBAL EXTRACTS**

5.1 Importance of Multi-Technique Approach to the investigation for Calculi

5.2 Detailed Analysis of the Effect of RAL Inhibitor on Crystal Size, Color, and Morphology

5.3 Raman Spectroscopic Characterization

5.4 Fourier Transform Infrared (FT-IR) Spectroscopic Characterization

5.5 X-ray Photoelectron Spectroscopic (XPS) Characterization

5.6 Photoluminescence (PL) Spectroscopic Characterization

5.7 Concluding Remarks
Chapter 6  CONCLUSIONS AND FUTURE WORK

6.1  L-arginine Doped Potassium Dihydrogen Phosphate (KDP) crystals

6.2  Growth and inhibition of calculi stone based on a traditional medicine approach with herbal extracts

References

Curriculum Vitae
List of Tables

Table 2.1: Physiochemical Properties of Some Inorganic NLO Materials.................................25

Table 2.2: Physiochemical Properties of Some Inorganic NLO Materials.................................29

Table 2.3: Physiochemical Properties of Some Semiorganic NLO Materials............................33

Table 2.4: Composition of Urinary Calculi (Courtesy: O.W. Moe97).........................................41

Table 4.1: The assignment of the infrared vibrational lines of pure KDP
(In 400 - 1600 cm\(^{-1}\))........................................................................................................104

Table 4.2: The assignment of the infrared vibrational lines of L-arginine
(In 400 - 1600 cm\(^{-1}\))........................................................................................................104

Table 4.3: The assignment of the infrared vibrational lines of L-arginine
doped KDP (In 400 - 1600 cm\(^{-1}\)) .......................................................................................104

Table 4.4: The assignment of the infrared vibrational lines of pure KDP
(In 2000 - 3600 cm\(^{-1}\))........................................................................................................107

Table 4.5: The assignment of the infrared vibrational lines of L-arginine
(In 2000 - 3600 cm\(^{-1}\))........................................................................................................107

Table 4.6: The assignment of the infrared vibrational lines of L-arginine
doped KDP (In 2000 - 3600 cm\(^{-1}\)).......................................................................................108

Table 4.7: The assignment of the Raman vibrational lines of pure KDP
(In lower frequency region)........................................................................................................114

Table 4.8: The assignment of the Raman vibrational lines of L-arginine
(In lower frequency region)........................................................................................................114
Table 4.9  The assignment of the Raman vibrational lines of L-arginine
doped KDP (In lower frequency region)..............................................115

Table 4.10  The assignment of the Raman vibrational lines of L-arginine
(In higher frequency region)..............................................................117

Table 4.11  The assignment of the Raman vibrational lines of L-arginine
doped KDP (In higher frequency region).............................................117
List of Figures

Figure 2.1(a) Linear optical behavior.................................................................11
Figure 2.1(b) Molecular energy levels...............................................................11
Figure 2.2(a) Non linear optical behavior.......................................................12
Figure 2.2(b) Molecular energy levels.............................................................12
Figure 2.3 Schematic presentation of the motion of bound charges in a dielectric medium. The motion of the ions is significant greater then the electrons. (from, The elements of Nonlinear Optics, Butcher. P. N. et al)...............................................................14
Figure 2.4 The effect of a nonlinear dependence of the polarization P on the electric field E. (from The elements of Nonlinear Optics, Butcher. P. N. et al)...............................................................18
Figure 2.5 Schematic representation of second harmonic generation...............20
Figure 2.6 KDP Crystal Structure and Growth Morphology (Courtesy: Ref 19)........27
Figure 2.7 Schematic representations of the amino acids...............................30
Figure 2.8 Schematic representation of L-arginine..........................................30
Figure 2.9 Schematic representations of urinary stone in urinary tract. (Courtesy: http://www.medicinenet.com/kidney)...............................................................34
Figure 2.10 Number of yearly stone discharges (1997-2002) (Courtesy: C. D. Scales et al. “Chnaging gender prevalence of stone disease”, J. of Urol. 177, 979-982 (2007)........38
Figure 2.11 Number of yearly calculi discharges by gender (1997-2002) (Courtesy: C. D. Scales et al. “Chnaging gender prevalence of stone disease”, J. of Urol. 177, 979 -982 (2007)..........................38
Figure 2.12 Struvite - Staghorn Calculi (Courtesy; eMedicine.com/Struvite)........42
Figure 3.1 General schematic of crystallizer used for rapid crystal growth........52
Figure 3.2  Crystal growth set-up for slow evaporation and slow cooling technique……..55
Figure 3.3  Illustrations of: (a) pure KDP crystals; (b) 0.3 wt.% L–arginine doped KDP crystal; (c) 0.4 wt.% L–arginine doped KDP crystal; and (d) 0.5 wt.% L–arginine doped KDP crystal…………………………………………………………………………………………….56
Figure 3.4  Test tube technique………………………………………………………………62
Figure 3.5  U- tube techniques………………………………………………………………62
Figure 3.6  Modified gel growth technique……………………………………………………..63
Figure 3.7  Experimental set-up for solubility reduction method……………………………….65
Figure 3.8  Experimental set-up for electrolytic method………………………………………….65
Figure 3.9  (a) Pure struvite crystal (Bigger and White), (b) 1 wt% and (c) 2 wt% Rotula Aquatica Lour incorporated struvite………………………………………………………………………..67
Figure 3.10  (a) Experimental set-ups for Thermo Gravimetric Analysis (TGA)………………..68
Figure 3.10  (b) Complete view of experimental set-ups for Thermo Gravimetric Analysis...69
Figure 3.11  Scheme of Michelson spectrometer………………………………………………..70
Figure 3.12  Inelastic and elastic scattering of photon from a molecule. (courtesy of Horiba Jobin Yvon)……………………………………………………………………………………………………………………………………..72
Figure 3.13  Schematic representation of: (a) Stokes Raman scattering, (b) Rayleigh scattering, and (c) Anti-Stokes Raman scattering…………………………………………………………………………………………………………………………………74
Figure 3.14  Schematic representation of Rayleigh, Stokes and Anti-stokes lines……………….75
Figure 3.15  The dipole moment for symmetric and asymmetric stretch in CO₂……………76
Figure 3.16  The polarization for different vibrational motions of CO₂ molecule………………76
Figure 3.17  Bruker IFS 66v FT-IR spectrometer (courtesy Bruker Inc.)…………………………77
Figure 3.18 Optical diagram of the Bruker IFS66v FT-IR spectrometer and of the Bruker FRA106 FT-Raman system (courtesy Bruker Inc.) ................................................................. 78

Figure 3.19 An alpha 300 WITec confocal Raman system ................................................................. 80

Figure 3.20 Schematic of an alpha 300 WITec confocal Raman system .................................................. 80

Figure 3.21 Energy diagram for XPS phenomenon ................................................................................. 84

Figure 3.22 Characteristic XPS spectrum ............................................................................................... 85

Figure 3.23 Schematic representation of XPS instrumentation ................................................................. 86

Figure 3.24 Typical experimental set-up for PL measurements ............................................................... 92

Figure 3.25 Horiba Jobin Yvon INDURAM spectrometer ....................................................................... 97

Figure 3.26 Optical diagram for Horiba Jobin Yvon INDURAM system .................................................. 98

Figure 4.1 FT-IR spectra for pure and 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped KDP crystals as labeled ........................................................................................................... 101

Figure 4.2 Infrared transmission data between 400 and 2000 cm\(^{-1}\) for (a) standard KDP and 0.5 wt% L-arginine doped KDP crystals, and (b) L-arginine reference sample ........................................... 102

Figure 4.3 Infrared transmission data in the 2200 - 3600 cm\(^{-1}\) range for: (a) standard KDP and 0.5 wt% L-arginine doped KDP crystals, and (b) L-arginine reference sample ........................................... 106

Figure 4.4 Comparison for L-arginine reference sample of (a) experimental infrared transmission spectrum and calculated infrared absorption spectrum, and (b) experimental and calculated Raman spectra ........................................................................................................... 109

Figure 4.5 FT-Raman spectra of 0.5 wt% L-arginine doped KDP crystal recorded at different spots on the sample .................................................................................................................. 110

Figure 4.6: Lower frequency region comparison of Raman spectrum of L-arginine doped KDP sample with Raman spectra of reference samples ........................................................................... 111
Figure 4.7  Higher frequency region comparison of Raman spectrum of L-arginine doped KDP sample with Raman spectra of reference samples..........................116

Figure 4.8  Schematic representations of possible interactions between L-arginine and KDP in the doped sample. (a) Hydrogen bonding between O\(^-\) of KDP phosphate unit and NH\(_3^+\) of L-arginine guanidyl group. (b) Similar hydrogen bonding between KDP phosphate O\(^-\) and L-arginine amino NH\(_3^+\).................................................................118

Figure 4.9  Thermogram of pure KDP crystals...............................................................120

Figure 4.10  Thermogram of 0.3 wt% L-arginine doped KDP crystals.......................121

Figure 4.11  Thermogram of 0.4 wt% L-arginine doped KDP crystals.......................121

Figure 4.12  Theromgram of 0.5 wt% L-arginine doped KDP crystals.......................122

Figure 4.13:  Thermograms for pure, 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped KDP crystals......................................................................................................................123

Figure 5.1  Pure, 1% and 2% RAL incorporated struvite crystals...............................127

Figure 5.2  Raman spectra of crystals without and with 1% and 2% inhibitor, as labeled..130

Figure 5.3  Transmission measurements of crystals without and with 2% inhibitor, as labeled..........................................................................................................................133

Figure 5.4  XPS survey scans for the crystals without and with 1% inhibitor in the binding energy range from 0 to 1100 eV.................................................................135

Figure 5.5  XPS spectra of: (a) Zn 2p\(_{3/2}\); (b) P 2p; (c) Mg 2s; (d) O 1s; (e) N 1s; and (f) C 1s, the key elements. In all graphs the bottom spectrum is that of the pure crystal and the top spectrum is that of the crystal with 1% inhibitor.........................................................136

Figure 5.6  Photoluminescence spectra of crystals without and with 1% and 2% inhibitor, as labeled.................................................................................................................140
CHAPTER 1

INTRODUCTION

1.1. Research Motivation

1.1.1. L-arginine doped Potassium Dihydrogen Phosphate (KDP) crystals

In materials engineering, the design of noncentrosymmetric crystals, which are crystalline materials without a center of inversion, is one of the fastest growing areas due to the extensive need for nonlinear optics (NLO) optical materials [1] in the fields of telecommunication and information devices. These materials play a vital role in the emerging photonics and optoelectronics technologies. Consequently, nonlinear optical frequency conversion materials have attracted significant attention and interest in conjunction with the advent of numerous of devices utilizing solid state laser sources which have had a significant impact on laser technology, optical communication and optical data storage [2-5].

The nonlinear relation between the refractive index and the applied electric field is used in nonlinear optical materials in order to produce different frequencies. This results in either harmonic generation such as frequency doubling, tripling, quadrupling, mixing etc., or frequency shifting such as optical parametric oscillation. Since laser beams exhibit the required energy density for producing nonlinear effects, development in the field of nonlinear optics improved in parallel with the invention of lasers [6].

Electro-optical materials, which are used for light modulation, Q-switching, and isolators, and photorefractive materials, also fall into the class of nonlinear optical materials. These
materials are utilized for the production of repetitive modulation as well as for the generation of short pulses.

From the beginning days of lasers the benefit of nonlinear optical materials was clearly evident, since they expanded the spectral regime of laser operation. Initially this was done by frequency doubling, followed by tripling of the Nd-laser (1064nm) frequency into the green (532 nm). Other opportunities were found with the invention of optical parametric oscillation, which allows shifting of coherent radiation to higher wavelengths [7]. Ideal materials for these types of applications should exhibit a large nonlinear coefficient for frequency conversion, large transparency range, high laser damage threshold, fast optical response time, mechanical stability and chemical inertness, and architectural flexibility for molecular design and morphology [2,7]. Nowadays, for certain wavelengths, numerous nonlinear optical materials are available with different optical characteristics and thresholds. However, there are very few materials which satisfy most of the requirements. As a result, the search for new materials seems to be endless [8].

Generally, most inorganic crystals exhibit certain properties such as high damage threshold, good transparency, chemical stability, and good hardness. For example, the discoveries of inorganic crystals such as Ammonium Dihydrogen Phosphate (ADP), Potassium Dihydrogen Phosphate (KDP) and Lithium Niobate (LiNbO$_3$) during the last thirty years have played an important role in the major areas of laser science and nonlinear optics .

Also, organic materials are emerging as an alternative to inorganic materials for their use in nonlinear optics and devices. The superiority of organic NLO materials results from their versatility and the possibility of tailoring them for a particular device application. Furthermore, they exhibit efficient molecular nonlinearity over a broad frequency range, low cost, low
dielectric constant, inherent synthetic flexibility, high optical damage threshold, and ultrafast response [9-10]. Several organic NLO materials with large NLO coefficients have been developed during the last 15 years [11]. On the other hand, most of the organic NLO materials exhibit certain drawbacks such as poor mechanical and thermal properties and susceptibility to damage during processing. Also, for device applications, large quality crystals of organic materials are necessary, which is a nontrivial requirement [12]. Furthermore, most of the organic crystals absorb in the blue light region, with an approximate cut-off wavelength exceeding 450 nm. While using a semiconductor laser within the 800nm band, this cut-off wavelength could reduce the conversion efficiency of second harmonic generation (SHG) due to the material self-absorption [13].

Thus, organic and inorganic compounds both have their respective advantages and disadvantages. So, scientists came up with new ideas in order to overcome the inherent limitations on the maximum attainable nonlinearity in inorganic materials and the limited success in growing device-grade organic single crystals. These, of course, entailed developing hybrid inorganic-organic nonlinear optical materials with little trade-off in the respective advantages of the two different types. This new class of NLO materials is also sometimes referred to as the semiorganic nonlinear optical materials [8,11,14-16].

One of the goals of this thesis is to achieve a detailed characterization of such organic-inorganic composite NLO materials based on amino-acid (L-arginine) doped Potassium Dihydrogen Phosphate (KDP) crystals. Investigation of standard inorganic KDP nonlinear optical material is performed, too.

Potassium Dihydrogen Phosphate not only has a high laser damage threshold and a large nonlinear optical coefficient, but also exhibits the advantages of good structural quality and
mechanical properties. These unique properties make KDP crystals ideal candidates for NLO applications, and, hence, they have been extensively used for frequency conversion, Q switches and shutters for high speed photography [17-18].

On the other hand, α–amino acids proved to be ideal candidates for NLO applications because they have certain special characteristics, such as molecular chirality, weak Vander Waals and hydrogen bonds, and absence of strongly conjugated bonds. They also exhibit wide transparency ranges in the visible and UV spectral regions. Moreover, they possess a zwitterionic molecular character, which favors crystal hardness [19]. Therefore, doping KDP crystals with amino acid families has been under extensive investigation in recent times owing to favorable enhancement of the NLO properties of standard KDP crystals [20, 21]. Recent research on the effectiveness of doped NLO materials demonstrates that L-arginine based crystals are worthy candidates, with outstanding optical, thermal and mechanical properties [20, 22].

In the present study, pure and 0.3 wt%, 0.4 wt%, as well as 0.5 wt% L-arginine doped KDP crystals were grown using solution growth techniques and further subjected to powder X-ray diffraction (XRD) measurements for crystal structure determination and to infrared (IR) absorption and Raman studies for confirmation of chemical group functionalization for investigating the incorporation mechanism of the L-arginine organic material into the KDP crystal structure. A prediction of possible incorporation mechanisms of the organic material was obtained from comparison of the simulated infrared and Raman vibrational spectra (achieved through a Gaussian software) with the experimental results. The effect of L-arginine doping on the thermal stability of the grown KDP crystal was also studied through Thermo gravimetric analysis (TGA)
1.1.2. Kidney stone formation and its inhibition by herbal extracts

Since urinary stones are one of the oldest and the most widely spread diseases, it is a serious health problem not only for humans but also for animals and birds. Stone formation in the kidney is also considered one of the most painful diseases of the urinary tract [23]. Urolithiasis is an universal problem regardless of geographical, cultural or racial groups. For example, according to one estimate, every year 600,000 Americans suffer from urinary stones and approximately 10-15% of the residents of the developed countries may be diagnosed with kidney stone disease. 20-25% of the residents of the Middle East may be diagnosed with kidney stone disease.

The financial costs for diagnosis and treatment of kidney stones are shocking. For example, in the United States, roughly $2 billion dollars were spent for this type of treatment during 1993. Also, several reports have indicated that the prevalence of kidney stone disease in westernized countries has been increasing [24-26].

Although significant knowledge about kidney stones has been acquired, their recurrences demonstrate that this phenomenon is quite complex and cannot be eliminated. It is believed that kidney stones are formed due to mineral super-saturation and crystallization in the urine. However, the exact causes of kidney stone formation are not completely known yet [27]. While possible factors in their formation are heredity, environment, age, sex, urinary infection, diet, and metabolic diseases, there are still lots of unanswered questions related to efficient inhibition and treatment mechanisms, even after considerable investigation. As a result, not a single hypothesis exists today that can associate explicitly these metabolic abnormalities with a common pathological mechanism. In this context, every new insight into this matter is valuable.
Calcium Oxalate and Calcium Phosphate stones are the most common component of nephrolithiasis, i.e. kidney stones. Magnesium Ammonium Phosphate calculi (MgNH₄PO₄·6H₂O), also called “struvites”, usually appear in the setting of urinary tract infections, from where their second name as “infection stones” is derived. They are also the most common type of renal stone [28].

Many remedies have been employed through the ages for the treatment of urinary stones. Modern curative measures reflect the current advances and are based on surgical removal, percutaneous techniques and extracorporeal shock wave lithotripsy (ESWL). Though these procedures prove to be useful, they are quite expensive for most people. Recurrence of these diseases is very common with these procedures and the patients have to be subjected to careful follow up for several years [29].

On the other hand, in traditional therapeutic systems, most of the remedies were taken from plants and they proved to be useful. However, the rationale behind their use is not thoroughly established through systematic pharmacological and clinical studies. Since possible curative merits have come to light lately, it has been demonstrated in various pharmacological and clinical reviews that the plant extracts exhibit antiurolithiatic activity and thus they can indeed reduce the occurrence of urinary calculi [29-30]. Following this, several researchers were inspired to analyze different herbal formulations from the chemical perspective [29-39]. These studies were carried out for various plants such as Tamrindus indica Lour [30], Ammania baccifera [31], Homonia riparia [34], Rotula Aquatica Lour [35, 36], Aerva lanata [37], Vediuppu chunam [37], Phyllanthus niruri [38], and Mimosa pudica [39], to mention only a few. However, due to destructive chemical methods, no consensus about the exact nature of the reactions taking place exists to date. Moreover, according to the literature wide varieties of plants
are useful for the cure and prevention of kidney stones, indicating that it would be advantageous to explore many other plants for potentially curative applications.

In this regard, in an attempt to achieve more insights, we propose a detailed scientific study of kidney stone formation and growth inhibition based on a traditional medicine approach with herbal extracts. In the present work, spectroscopic investigations of these processes were performed through different techniques. Raman, infrared absorption, X-ray photoelectron spectroscopy (XPS), and photoluminescence were used in order to analyze the effects of *Rotula Aquatica Lour* (RAL) on the growth of manganese-based calculi. Our research work might serve as an important source of information on this tantalizing and complex problem, which is not completely understood so far.

1.2. Dissertation outline

This dissertation encompasses two phases of research project. In the first phase of research project, the spectroscopic and thermal studies have been carried out of hybrid inorganic-organic nonlinear material i.e. L-arginine doped KDP crystals. In the second phase of my project, I performed a detailed scientific study of kidney stone formation and growth inhibition based on a traditional medicine approach with herbal extracts.

In the first section of chapter 2, the concept and physics of nonlinear optics is described briefly followed by the importance of materials properties in terms of nonlinear optical device applications. In this section importance and applications of nonlinear optics and second harmonic generation are also discussed. Moreover, superiority and inferiority of both organic and inorganic materials are discussed followed by the importance of hybrid organic-inorganic (semi-organic) nonlinear optical materials. Finally, an attempt is made to provide justification for our
choice of the materials (i.e KDP and L-arginine) and research project by explaining their exceptional properties in terms of nonlinear optical applications.

In second part of the chapter 2, an attempt is made to explain the significance of the present study of renal calculi by describing general causes for the formation of calculi, history of calculi and the universality of it. In this chapter different types of kidney stones and their compositions are also described. Finally, the justification for the scientific study of traditional medicinal approach is also discussed.

The first phase of chapter 3, briefly describes different crystal growth techniques and their respective advantages and disadvantages. The solution growth technique and experimental set-up, which was used to grow the pure and L-arginine doped crystals for the present study, is also explained. Moreover, explanation of different characterization techniques employed for the analysis of the grown crystals is also provided in this section. The pros and cons of the respective techniques are also discussed. Experimental set-ups for Fourier transform infrared (FTIR) absorption, Raman spectroscopy and Thermo gravimetric analysis (TGA) are demonstrated followed by their description.

The second segment of chapter 3 provides the explanation of the gel growth technique utilized to grow the pure *Magnesium Ammonium Phosphate* (struvite) and *Rotula Aquatica Lour* (RAL) incorporated struvite crystals for the present study. In this section, *X-ray photoelectron spectroscopy* (XPS) and Photoluminescence are described followed by the explanation of Gauss simulation software. Moreover, experimental set-ups are also demonstrated and discussed for multiple spectroscopic techniques such as infrared, Raman, XPS and photoluminescence.

The chapter 4, not only the outcome of the different characterization techniques is described but also their significance is discussed for the L-arginine doped KDP crystals.
The chapter 5, the results of different characterizations is discussed for the pure and inhibitor incorporated calculi crystals.

In the first part of chapter 6, we have summarized our conclusion and future work for L-arginine doped KDP crystals and in the second part of chapter 6, we have summarized our conclusion and future work for the pure and $LAR$ inhibitor incorporated kidney stones.
CHAPTER 2

THEORETICAL BACKGROUND

2.1. Introduction to nonlinear optical materials

2.1.1. Highlights of nonlinear optics

In optics we are concerned with the interaction of light with matter. The optical properties of materials are quite independent of the intensity of illumination for the relatively low light intensities that generally occur in nature. The optical properties of matter that are familiar to us through our visual sense are those in which light waves are able to penetrate and pass through a medium without any interaction between the waves. However, in the case of sufficiently intense illumination, the optical properties start to depend on the intensity and other characteristics of the light. In such cases, light waves may interact with each other as well as with the medium. This is the realm of nonlinear optics (NLO). The output from a coherent light source such as a laser can be used to attain the intensities needed to observe these effects. Such behavior is utilized to great effect in nonlinear optical devices and techniques which have important applications in many branches of science and engineering, and provides insight into the structure and properties of matter [40].

Nonlinear optical phenomena are not part of our everyday experience. Their discovery and development were possible only after the invention of the laser.

Nonlinear optics has many applications in a variety of fields, such as the frequency doubling of semiconductor lasers, the generation of ultrashort laser pulses, dispersion
compensation in communication systems, and all-optical switching [41]. Nonlinear optics plays a vital role in emerging photonics and optoelectronics technologies, and in information processing and telecommunication devices [42-45].

2.1.2. Linear versus nonlinear optics

Generally, most optical processes such as transmission, reflection, refraction, superposition and birefringence, fall in the category of what is called linear optics. In linear optics it is assumed that an optical disturbance propagating through an optical medium can be described by a linear wave equation (see Figure 2.1). Based on this assumption, two harmonic waves traveling without distortion in a medium follow the principle of superposition. The mutual interference of the waves is a phenomenon determined by the medium itself, regardless of the intensity of the light. In order to describe the behavior of a light beam in a transparent material, only the wavelength and velocity are required [46].

**Figure 2.1(a):** Linear optical behavior. **Figure 2.1(b):** Molecular energy levels.

When the incident light intensity becomes high enough, linear optics is not sufficient to describe the resultant phenomena. The invention of the laser made it possible to have more intense and coherent light. With the help of such intense and coherent light, it was observed that
certain optical properties of material media, such as refractive index, become a function of the electric field of the light. In this case, the principle of superposition no longer holds. Two or more light waves interact with one another and with the medium (see Figure 2.2). These situations provide examples of nonlinear optical phenomena. In order to describe such nonlinear phenomena an extension of the linear theory is required which allows for a nonlinear response of optical materials to the electromagnetic radiation [46].

**Figure 2.2(a):** Nonlinear optical behavior.  
**Figure 2.2(b):** Molecular energy levels.

### 2.1.3. **Origin of optical nonlinearity**

An optical material can be considered as a collection of charged particles: electrons and ion cores, which tend to move in an applied electric field. The positive charges move in the direction of the field, while the negative charges move in the opposite direction. If an electric field is applied to a conductor, some of the charged particles that move freely through the material increase the flow of the electric current. However, in dielectric materials, since the charged particles are bound together (although the bonds do possess certain ‘elasticity’), the
motion of the charges is transitory when the field is first applied; they are displaced slightly from their usual positions. This small movement of positive and negative charges in opposite directions results in a collection of induced electric-dipole moments. In other words, the induced polarization exists due to the effect of the field on a dielectric medium [40].

A light wave possesses electric as well as magnetic fields varying sinusoidally at ‘optical’ frequencies. Thus, the motion of the charged particles in a dielectric medium in response to an optical electric field is oscillatory; they form oscillating dipoles. Generally, the effect of the optical magnetic field on the particles is neglected because it is too weak. Also, for high optical frequencies, only the motion of electrons is significant. This is due to the much greater mass of the positively charged particles.

The response of an electron to the optical electric field is that of a particle in an anharmonic potential well. We can think of this in terms of a simple mechanical analogy. Let us consider that the electron with mass m and charge –e is attached to another ion by a spring, as shown in Figure 2.3. For simplicity, consider the scenario shown where all electric dipoles are oriented in the direction of the field.

Nonlinear phenomena are ultimately due to the inability of the dipoles in an optical medium to respond in a linear fashion to the alternating $\vec{E}$-field associated with a light beam. The atomic nuclei are too massive and the inner-core electrons too strongly bound to respond to the alternating $\vec{E}$-field at the frequency of light. Thus, only the outer electrons of the atoms in a material are primarily responsible for the polarization of the optical medium by the $\vec{E}$-field. In the case of small oscillations of these electrons, the polarization is proportional to the $\vec{E}$-field. However, just like the harmonic oscillations of a simple spring, which become increasingly
anharmonic with increased oscillation amplitude, this proportionality starts to fail with an increase in the strength of the $E$-field.

**Figure 2.3:** Schematic presentation of the motion of bound charges in a dielectric medium. The motion of the ions is significant greater than the electrons. (from *The elements of Nonlinear Optics*, Butcher. P. N. *et al*).

Another means of exciting nonlinear behavior without using high beam irradiances is to choose the exciting optical frequency near a resonant frequency of the oscillating dipoles. This technique is widely utilized in *nonlinear spectroscopy* and is known as *resonance enhancement* [46].

The polarization of a linear medium by an electric field $\vec{E}$ can be written as,

$$\vec{P} = \varepsilon_0\chi \vec{E}$$  \hspace{1cm} (1)

Where $\chi$ is the susceptibility coefficient and $\varepsilon_0$ is the vacuum permittivity.
For a small nonlinearity, the modification of the susceptibility in a nonlinear medium can be represented by a power series as follows:

\[
\chi = \chi_1 + \chi_2 E + \chi_3 E^2 + .......
\]  

(2)

Substituting the value of equation (2) into equation (1), the polarization strengths can be given by:

\[
P = \varepsilon_0 (\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + .......) 
\]

(3)

or

\[
P = P_1 + (P_2 + P_3 + .......) 
\]

(4)

\[\begin{align*}
\text{linear} & \quad \text{small nonlinear terms}
\end{align*}\]

The optical properties of the medium can be characterized by the linear and nonlinear susceptibility coefficients. This relation between \( P \) and \( E \) completely characterizes the response of the optical medium to the field [46].

Since the susceptibility of the medium usually is defined as \( \chi = \varepsilon_0 \chi_1 \), in linear media, only the \( \chi_1 \) contribution is important. Thus, in linear optics, the polarization of a medium is simply proportional to the electric field and is represented only by the first term \( P_1 \) in equation (3), e.g. \( P_1 = \varepsilon E \). If the amplitude of electric field is not large enough the \( \chi \) coefficients of the higher powers of \( E \) are too small to allow them to significantly influence the polarization. These higher order terms start to play an important role only for very intense and coherent light. To this end, the high coherence of the laser light, which allows the beam to be focused onto small spots, locally produces electric field strengths exceeding \( 10^{10} \) V/m, which is on the order of the field strengths binding electrons to nuclei in an optical medium.

Now, the question is how large the incident optical field must be to allow atoms and molecules to demonstrate their nonlinear properties. To this point, from the above discussion it is
clear that, in order to observe considerable nonlinearity arising from the anharmonic motion of electrons, we require an incident field which is not completely insignificant in comparison with the internal field (which is of the order of $10^{10}$ V/m.). An incident intensity of $\sim 10^{14}$ W/cm$^2$ is required in order to obtain an optical field of such magnitude and this can be achieved by focusing the powerful picosecond duration pulses from mode locked lasers. However, in reality such high intensities are not required in many nonlinear optical effects and this is because of ‘phase matching’ [40].

For example, for significant second-harmonic generation under phase-matched conditions the characteristic length can be expressed as,

$$L \sim \frac{\lambda E_a}{E}$$

(5)

where $E$ is the incident optical field, $E_a \approx 10^{10}$ V/m, and $\lambda$ is wavelength of the incident optical field.

So, if we substitute $\lambda=1$ µm and power density of 1 MW/cm$^2$ (i.e. incident field $\sim 10^6$ V/m) we will get $L \sim 1$ cm. Intensity of such magnitude can readily be achieved by the use of a modestly sized pulsed laser.

2.1.4. Brief history

The history of nonlinear optics can be thought of as being either brief or long depending on one’s frame of reference. In fact, before the beginning of the 20th century, the first studies of the linear electrooptic effect were performed. But here we only restrict our focus to second harmonic generation or other optical frequency mixing processes; then the history is not older than 1961, when second harmonic generation (SHG) was observed [47].

In 1961 at the University of Michigan, Peter Franken [48] and his coworkers demonstrated the first nonlinear coherent optics experiment. They focused the coherent 694.3 nm
output from a pulsed ruby laser onto a quartz crystal and detected in the output the presence of a weak ultraviolet coherent radiation component at 347.15 nm, which being twice the frequency or half the wavelength of the exciting light is the second harmonic [46].

There are several phenomena which are associated with nonlinear optics. These can be classified according to the exponent of the nonlinearity as listed below [49].

1. Second-Order Effects
   - Second Harmonic Generation (SHG)
   - Pockel’s effect
   - Optical parameter amplification
   - Electro-optical beam deflection
   - Optical rectification

2. Third-Order Effects
   - Third Harmonic Generation (THG)
   - Kerr effect –induced birefringence
   - Self-focusing
   - Self-diffraction
   - Self-phase modulation
   - Solitons
   - Four-wave mixing (FWM)
   - Stimulated Brillouin scattering (SBS)
   - Optical Phase Conjugation (PC)
2.1.5. **Second harmonic generation and frequency mixing**

Second harmonic generation is the contribution of the second order term in the equation (3), namely

\[ P_2 \equiv \varepsilon_0 \chi_2 E^2 \]  

(6)

In this case, the second order polarization term \( P_2 \) of the optical medium is proportional to the square of the electric field. The polarization as a function of the electric field for the linear case and the deviation from linearity due to this second order term is demonstrated in **Figure 2.4**.

![Figure 2.4](image)

**Figure 2.4**: The effect of a nonlinear dependence of the polarization \( P \) on the electric field \( E \).

(from *The elements of Nonlinear Optics*, Butcher P.N. et al)

For an isotropic optical material or for one having a center of symmetry it can be shown that the second order term has is vanishing in the polarization expansion. A crystal having a center of symmetry is characterized by an inversion center. Therefore, if the radial coordinate \( r \) is changed to \( -r \) the crystal’s atomic arrangement remains unchanged, and so, the crystal responds in the same way to a physical influence. In such a crystal, reversing the applied field should not change any physical property such as its susceptibility.
Thus, we should have both $P_2 \equiv \varepsilon_0 \chi_2 (+E)^2$ and $-P_2 \equiv \varepsilon_0 \chi_2 (-E)^2$.

Because the $\vec{E}$ - field is squared, $P_2 = -P_2$, which can only be true if $P_2 = 0$.

The quartz crystals used by Franken, as well as many other crystals, do not possess inversion symmetry. Consequently, they can readily exhibit second harmonic generation in addition to other second-order phenomena.

The existence of a second harmonic in the polarization is expected from the following mathematical argument: if the applied electric field, or one of its Fourier components, is of the form

$$E = E_0 \cos \omega t$$

(7)

By using the equation (7) in the equation (5)

$$P_2 = \varepsilon_0 \chi_2 E_0^2 \cos^2 \omega t = \varepsilon_0 \chi_2 E_0^2 \left[ \frac{1 + \cos 2\omega t}{2} \right] \Rightarrow P_2 = \frac{1}{2} \varepsilon_0 \chi_2 E_0^2 \cos 2\omega t$$

(8)

In short, the second order polarization $P_2$ possesses a term of twice the frequency of the applied optical field, together with a constant or a DC component that represents optical rectification. Optical rectification results in a time independent polarization in the medium that manifests itself as a DC voltage across the nonlinear crystal, in a transverse direction to the field propagation. The component of $P_2$ oscillating at $2\omega$ corresponds to the dipole oscillations in the medium with the same frequency. The electromagnetic radiation of angular frequency $2\omega$ generated by these dipole oscillations, is present in the resultant field together with a stronger first-order field at the fundamental frequency $\omega$. For example, as schematically presented in Figure 2.5, second harmonic generation is commonly used to produce light of wavelength 532 nm by passing the 1064-nm light produced by a Nd:YAG laser through a nonlinear crystal.
A few applications established in a variety of technological fields based on nonlinear optics are:

- Optical phase conjugation
- Optical parametric oscillators
- Optical computing
- Optical switching
- Optical data storage

2.1.6. Materials point of view

Before any experiments were carried out, it was known theoretically that the crystal should not have a center of inversion. It was also clear that the symmetry requirements for second harmonic generation and piezoelectricity were the same. Additionally, it was required that the crystal be transparent for all frequencies involved in the interaction. Moreover, it should be thermally stable and it should exhibit good optical properties, i.e., large optical damage threshold, large birefringence. Since, quartz was readily available in large, perfect single crystals, Franken and his co-workers used quartz when they made experimental observations of SHG [49-50].
In the field of nonlinear optics, progress has always been dictated by the accessibility of improved and newer material from the day of the first demonstration of second harmonic generation (SHG) in quartz by Franken et al. The conversion efficiency of the second harmonic generation process is given by \[51-53\]

\[
\eta_{\text{SHG}} = \frac{P_{2\omega}}{P_{\omega}} = 2 \left( \frac{\mu}{\varepsilon_0} \right)^{1/2} \frac{\sigma^2 d^2 l^2}{n^3} \sin^2 \left( \frac{\Delta k l}{2} \right) \frac{P_{\omega}}{(\Delta k l / 2)^2 A} \tag{9}
\]

where \(d\) is the effective nonlinear coefficient, \(n\) is the refractive index, \(k\) is the wave vector, \(\varepsilon_0\) is the vacuum permittivity, \(P\) is the power and \(A\) is the area.

Since, for a specific material and for a certain frequency \((\omega)\) the conversion efficiency is directly proportional to the square of the interaction length \(l\), it is imperative to have large crystals. The maximum usable length of the crystal is limited to a few microns due to the interference from the input fundamental polarization wave and the driven harmonic polarization wave. However, by the action of “phase matching” \((i.e.\ by\ decreasing\ \Delta k\ to\ zero)\) this problem could be resolved. The term \(d^2/n^3\) is referred to as the figure of merit for SHG. This is the characteristic of the material that often merits first consideration in the search for newer materials. By increasing the power density \((P_{\omega} / A)\) of the input beam, the conversion efficiency can be further improved for a chosen material and selected interaction geometry. This can be physically achieved by focusing the beam into the crystal, increasing the power densities to the tolerance limit, called the “damage threshold”.
2.1.6.1 *Importance of laser damage threshold value*

Nonlinear crystals are extensively used in laser engineering for different applications, which include modulation, Q-switching and frequency conversion. The operation of nonlinear devices generally involves the exposure of these materials to high power laser sources, especially in the case of frequency conversion. Thus, to determine the materials’ optical strength by exposing them intentionally to intense laser radiation is very important. While evaluating the potential usefulness of NLO materials, optical damage threshold must be considered together with the nonlinear susceptibility tensor, which limits the maximum efficiency of parametric process in nonlinear crystals. Laser-induced damage testing (LIDT) is extremely important in judging optical reliability in military systems. The laser sources utilized in range finders, designators, illuminators, lidar, and so on, are required to operate in unfavorable environments for long periods of time without adjustment or maintenance [54].

Moreover, the crystals must exhibit a few other additional physical properties, such as they must possess large transparency window, high melting point, mechanical stability and chemical inertness. Nowadays there are large numbers of non-linear optical materials for specific wavelengths, with various damage thresholds, and with various optical characteristics; however, it is extremely difficult to find the materials which satisfy most of these requirements. Hence, the search for new materials seems to be endless [52]

2.1.7. *Inorganic nonlinear optical materials*

During the early stages, since the physical properties of many inorganic materials are well studied, the materials explored for nonlinear optical applications had always been inorganic.
Inorganic materials can be synthesized quite easily because these materials are mostly ionically bonded. Generally, inorganic materials exhibit high melting points in addition to a high degree of chemical stability. High temperature oxide materials are well studied for different applications such as piezoelectricity, ferroelectricity and pyroelectricity. So, when the search for new materials began in NLO, scientists often trusted their intuition, screened the known materials, and were fairly successful. Some of the most useful crystals discovered are Lithium Niobate (LiNbO₃), Potassium Niobate (KNbO₃), Potassium Dihydrogen Phosphate (KDP), Potassium Titanyl Phosphate (KTiOPO₄) and Beta Barium Borate (BBO or β-BaB₂O₄). In fact, most of the commercial frequency doublers used currently are made of these inorganic materials. Some physiochemical properties for some well known inorganic materials are summarized in Table 2.1 [52]

Thus, inorganic materials exhibit various important properties such as high damage threshold, good transparency, and good hardness. Moreover they also exhibit good chemical stability. Hence, inorganic compounds have been extensively used for nonlinear optical applications. During the last thirty years, Ammonium Dihydrogen Phosphate (ADP), Potassium Dihydrogen Phosphate (KDP) and Lithium Niobate (LiNbO₃) have played a critical role in the major fields of laser science and nonlinear optics by proving their usefulness in many different optical applications.

Such materials were thus widely used as frequency multipliers for second and third harmonic generation for Nd:YAG (Neodymium doped Yttrium Alumina Garnet – Nd:Y₃Al₅O₁₂), and Nd:YLF (Neodymium doped Yttrium Lithium Fluoride- Nd:YLF₄) lasers. ADP as well as KDP are also used for electro-optical applications as Q-switches for Nd:YAG and Nd:YLF
lasers. Since these crystals are grown by a water solution method, they can be grown up to very large sizes; they are low-cost and large-sized nonlinear components.
Table 2.1: Physiochemical Properties of Some Inorganic NLO Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>LiNbO₃</th>
<th>KDP</th>
<th>β-BaB₂O₄</th>
<th>KTP</th>
<th>LiB₃O₅</th>
<th>KNbO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point group</td>
<td>3m</td>
<td>4 2m</td>
<td>3m</td>
<td>mm2</td>
<td>mm2</td>
<td>mm2</td>
</tr>
<tr>
<td>Transparency (nm)</td>
<td>350-5000</td>
<td>180-1800</td>
<td>198-2600</td>
<td>350-4500</td>
<td>160-2300</td>
<td>400-5500</td>
</tr>
<tr>
<td>Refractive Indices</td>
<td>nₒ= 2.2322</td>
<td>nₒ= 1.4931</td>
<td>nₒ= 1.6551</td>
<td>nₓ= 1.5737</td>
<td>nₓ= 1.5649</td>
<td>nₓ= 2.1194</td>
</tr>
<tr>
<td>(at 1064 nm)</td>
<td>nₑ= 2.1560</td>
<td>nₑ= 1.4582</td>
<td>nₑ= 1.5425</td>
<td>nᵧ= 1.7395</td>
<td>nᵧ= 1.5907</td>
<td>nᵧ= 2.2195</td>
</tr>
<tr>
<td>dₑff (pm/V)</td>
<td>5.1</td>
<td>0.35</td>
<td>1.6</td>
<td>3.2</td>
<td>0.85</td>
<td>13</td>
</tr>
<tr>
<td>Threshold Power (MW)</td>
<td>0.7</td>
<td>30</td>
<td>13</td>
<td>0.029</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Damage threshold (GW/cm²)</td>
<td>0.3 (10 nsec)</td>
<td>5 (1 nsec)</td>
<td>23 (14 nsec)</td>
<td>9-20 (1 nsec)</td>
<td>1-4 (12 nsec)</td>
<td>1 (10 nsec)</td>
</tr>
</tbody>
</table>

N.A.- Not Available
2.1.7.1. Potassium Dihydrogen Phosphate (KDP) crystals as NLO material

Potassium dihydrogen phosphate, as previously mentioned, being a NLO crystal, exhibits wide frequency conversion efficiency and a high damage threshold under high laser power. [55]. KDP and its isomorphic deuterated form, DKDP (KD$_2$PO$_4$), are interesting materials that have stimulated a great amount of interest amongst researchers due to their unique optical and mechanical properties. They are representative of hydrogen bonded material which possesses other important properties such as piezoelectricity and ferroelectricity. The crystallog-chemical analogue of KDP is established in quite a wide range of practical applications such as piezoelectric transducers in microphones, gramophones, and other sound reproduction devices [55 -56]. Due to its high laser damage threshold, large nonlinear optical coefficient, good structural quality, and mechanical properties, KDP has been also widely used for frequency conversion, Q switches and shutters for high speed photography [56-57].

Potassium dihydrogen phosphate belongs to the class $\bar{4}2_m$ of the tetragonal system with the space group $\bar{4}2d$ with 4 ‘molecules’ of KH$_2$PO$_4$ per unit cell. The unit cell dimensions are $a=b=7.434$ Å and $c = 6.945$ Å. [55, 59]. The structure is most easily pictured as built up from potassium atom phosphate groups. KDP crystal synthesized by using the solution growth technique is a tetragonal prism combined with a bipyramid. The prism faces are (100) and (010) planes and the prism axis is [001], as shown in Figure 2.6 [58]. Large KDP single crystals of the size of 40-55 cm and free from defects can be obtained at a fast growth rate of 10-20 mm/day. Thus, recently, their importance in electro-optics, harmonic generation, and inertial confinement fusion and on other fields has received renewed attention [57, 60-62].

Inorganic materials have thus played an important role as nonlinear optical materials. However, Bergman et al. in 1969 demonstrated that inorganic materials exhibit only a $\approx 20\%$
chance of eccentricity. Hence, in the search for newer materials with higher nonlinearity, inorganics have a reduced chance and advances have been limited [52]. In short, the application of inorganic compounds as NLO materials exhibits certain limitations.

2.1.8. Organic nonlinear optical materials

Organic materials are emerging as an alternative to inorganic materials because they possess better properties as compared to inorganic materials, such as efficient molecular nonlinearity over a broad frequency range, low cost, low dielectric constant, inherent synthetic flexibility, high optical damage threshold, ultrafast response with better processability, and ease of fabrication and integration into devices [63-69]. Organic compounds exhibit a high degree of delocalization because they are often formed by weak Van der Walls and hydrogen bonds. Hence, they are expected to possess better optical nonlinearity as compared with inorganic compounds. In optical signal processing, the required femtosecond ($10^{-15}$ sec) response time can be achieved through the use of organic materials. Moreover, organic polymeric materials exhibit

Figure 2.6: KDP Crystal Structure and Growth Morphology (Courtesy: Ref 58)
laser damage thresholds greater than 10 GW/cm$^2$ with picosecond pulses. The dielectric constants of organic materials are lower than those of inorganic crystals and thus allow the minimization of phase mismatch [65-66]. Some physiochemical properties for some well known organic materials are summarized in Table 2.2 [52].

Thus, over the past two decades, there has been a search for new NLO materials. Recent research work in quantum electronics is focused on finding new materials for efficient second harmonic electro-optic modulation, and a new class of promising nonlinear organic materials has emerged with superior qualities over inorganic materials [42, 63-70]. This class includes NLO organic molecules such as thiourea, 2-(alpha-Methylbenzylamino)-5-nitropyridine, Amino-3-nitropyridine, 2-Aminofluorene, 4-Nitroaniline, 5-Nitroindole, 5-Nitouracil, L-arginine phosphate monohydrate (LAP), etc. many of these have been investigated because of their large second or third order hyper-polarizability as compared with inorganic NLO materials [70]. An inexpensive low-temperature growth method is used for synthesizing good quality single crystals of such organic compounds.

2.1.8.1. L-arginine organic nonlinear optical material

There are about twenty-eight commonly known amino acids, which, combined in different ways, form other complex organic compounds (more than 40,000 proteins are known so far to science). Due to the presence of a chiral carbon, which is surrounded by four functional groups, and to the non-centro symmetric nature of the crystalline structure, all amino acids, except glycine, exhibit NLO properties. In the solid state, an amino acid exhibits a protonated amino group (NH$_3^+$) and a deprotonated carboxylic acid (COO$^-$) group. This dipolar nature of amino acids makes them ideal candidates for NLO applications (see Figure 2.7).
Table 2.2: Physiochemical Properties of Some Inorganic NLO Materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>MNA</th>
<th>POM</th>
<th>DAN</th>
<th>MMONS</th>
<th>MBANP</th>
<th>MAP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Point group</strong></td>
<td>mm2</td>
<td>222</td>
<td>2</td>
<td>mm2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>Melting point(°C)</strong></td>
<td>114</td>
<td>136</td>
<td>166</td>
<td>NA</td>
<td>84</td>
<td>80-9</td>
</tr>
<tr>
<td><strong>Transparency (nm)</strong></td>
<td>480-2000</td>
<td>500-1700</td>
<td>485-2700</td>
<td>510-2100</td>
<td>NA</td>
<td>500-2500</td>
</tr>
<tr>
<td><strong>Refractive Indices at 1064nm</strong></td>
<td>(n_x = 1.800)</td>
<td>1.663</td>
<td>1.517</td>
<td>1.530</td>
<td>1.650</td>
<td>1.507</td>
</tr>
<tr>
<td></td>
<td>(n_y = 1.600)</td>
<td>1.829</td>
<td>1.636</td>
<td>1.630</td>
<td>1.714</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>(n_z = ?)</td>
<td>1.625</td>
<td>1.843</td>
<td>1.961</td>
<td>1.688</td>
<td>1.843</td>
</tr>
<tr>
<td><strong>Nonlinear coefficient (x10^-9 esu)</strong></td>
<td>(d_{11} = 60)</td>
<td>(d_{14} = 23)</td>
<td>(d_{22} = 12.4)</td>
<td>(d_{24} = 55)</td>
<td>(d_{22} = 8.3)</td>
<td>(d_{21} = 40)</td>
</tr>
<tr>
<td></td>
<td>(d_{12} = 90)</td>
<td>(d_{25} = 23)</td>
<td>(d_{23} = 119)</td>
<td>(d_{32} = 41)</td>
<td>(d_{22} = 44)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(d_{36} = 23)</td>
<td>(d_{33} = 184)</td>
<td>(d_{33} = 8.8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Damage threshold (GM/cm²)</strong></td>
<td>0.2 (20 n sec)</td>
<td>2 (0-02 n sec)</td>
<td>5 (10 n sec)</td>
<td>NA (12 n sec)</td>
<td>1 (10 n sec)</td>
<td>3 (10 n sec)</td>
</tr>
</tbody>
</table>

**MNA**: 2-methyl-4-nitroaniline;  
**POM**: 3-methyl-4-nitropyridine-1-oxide;  
**DAN**: 4-(n,n-dimethylamino)-3-acetamido nitrobenzene;  
**MMONS**: 3-methyl-4-methoxy-4-nitrostilbene;  
**MBANP**: 2-(α-methylbenzyl-amino)-5-nitropyridine;  
**MAP**: metil-(2,4-dinitrophynyl)-amino-2-proponate.
Thus, in the organic category, α-amino acids possess precise features such as molecular chirality and weak van der Waals and hydrogen bonds, as well as the absence of strongly conjugated bonds. Additionally, they also exhibit wide transparency ranges in the visible and UV spectral regions, and good hardness due to the zwitterionic nature of the molecules [72]. Among the different types of amino acids, L-arginine - (NH₂C(NH)NH(CH₂)₃CH(NH₂)(COOH); is one type of amino acid; which is represented in Figure 2.8.
However, there has been little progress in fabricating devices out of these molecular crystals. Moreover, these crystals also exhibit numerous adverse physical parameters. Large dipole moment, which leads to large $\chi^{(2)}$, is also responsible for increased absorption at higher frequencies. Hence, most of these molecular materials have poor transparency and small transparency windows. Consequently, the general harmonic wave gets absorbed in the crystal, leading to poor efficiency. Also, organic NLO materials are inherently poor in mechanical hardness, and have low melting points and poor chemical inertness. Owing to the high polar nature of the molecules, they often tend to crystallize as long needles or thin platelets.

### 2.1.9. Hybrid organic-inorganic nonlinear optical materials

Scientists had to adopt newer strategies in order to overcome the inherent limitations on the maximum attainable nonlinearity in inorganic materials and the limited success in growing device-grade organic single crystals. Obviously, it was desirable to develop hybrid inorganic-organic materials with little trade-off in their respective advantages. This new class of materials is also known as the semiorganics [52, 73-75]. In the case of a hybrid inorganic-organic NLO material, the high optical nonlinearity of a purely organic material is combined with the favorable mechanical and thermal properties of an inorganic material. Hence, recently there has been considerable interest in the synthesis of hybrid inorganic-organic (semiorganic) nonlinear optical materials with excellent second – order optical nonlinearities.

Highly focused efforts have been made in the search for novel high quality nonlinear optical materials that can generate high second harmonic blue-violet light in the...
form of GaAlAs laser diodes. Coherent blue and green light is important for many applications such as display, high-resolution printing, and signal processing [51]. As we have observed, most organic NLO crystals usually possess poor mechanical and thermal properties and are susceptible to damage during processing. Moreover, it is difficult to grow large optical quality crystals of these materials for device applications. Hybrid inorganic-organic NLO crystals have good thermal and mechanical properties and large nonlinear coefficients.

Doping KDP crystals with amino acid families is under extensive investigation in recent times owing to favorable enhancement of NLO properties of standard KDP crystals [76]. The search for effective NLO materials demonstrates that L-arginine based crystals such as L-arginine phosphate monohydrate (LAP), which was first reported by Xu et al. [77], exhibit high non-linearity and conversion efficiency, wide transmission range, and high damage threshold [78]. As a consequence of this discovery, series of amino acid crystals such as L-arginine acetate (LAA) [79], L-arginine hydrobromide (LAHBr) [80], L-arginine hydrochloride (LAHCl) [81], L-arginine diphosphate (LADP) [82], L-arginine hydrofluoride (LAHF) [83], L-arginine dinitrate (LADN) [84], L-histidine hydrofluoride dehydrate (LHHF) [85] and L-histidine tetrafluoroborate (L-HFB) [86] have been investigated. All of these new crystals are reported to have better NLO properties compared to those of the well-known inorganic crystal of KDP.
Table: 2.3  Physiochemical properties of semiorganic NLO materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>dLAP</th>
<th>BTCC</th>
<th>ZTS</th>
<th>ATCC</th>
<th>ATMB</th>
<th>TSCCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point group</td>
<td>2</td>
<td>mm2</td>
<td>mm2</td>
<td>3m</td>
<td>3m</td>
<td>M</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>130</td>
<td>185</td>
<td>&gt;200</td>
<td>101</td>
<td>138</td>
<td>230</td>
</tr>
<tr>
<td>Transparency (nm)</td>
<td>250-1300</td>
<td>300-2000</td>
<td>300-2000</td>
<td>300-1500</td>
<td>330-1500</td>
<td>330-1420</td>
</tr>
<tr>
<td>Refractive</td>
<td>$n_x=1.49769$</td>
<td>$n_x=1.6097$</td>
<td>$n_x=1.6306$</td>
<td>$n_x=1.6996$</td>
<td>$n_x=1.7046$</td>
<td>$n_x=1.7200$</td>
</tr>
<tr>
<td>At 1064 nm</td>
<td>$n_y=1.5595$</td>
<td>$n_y=1.7902$</td>
<td>$n_y=1.6936$</td>
<td>$n_y=1.6400$</td>
<td>$n_y=1.6341$</td>
<td>$n_y=1.7180$</td>
</tr>
<tr>
<td>$n_z=1.5686$</td>
<td>$n_z=1.8600$</td>
<td>$n_z=1.984$</td>
<td>$n_z=1.984$</td>
<td>$n_z=1.984$</td>
<td>$n_z=1.984$</td>
<td>$n_z=1.984$</td>
</tr>
<tr>
<td>Nonlinear</td>
<td>$d_{14}=0.22$</td>
<td>$d_{31}=2.75$</td>
<td>$d_{31}=0.31$</td>
<td>$d_{31}=1.5$</td>
<td>$d_{31}=0.27$</td>
<td>$d_{11}=0.5$</td>
</tr>
<tr>
<td>Susceptibility</td>
<td>$d_{16}=0.48$</td>
<td>$d_{32}=0.2$</td>
<td>$d_{32}=0.7$</td>
<td>$d_{22}=8.2$</td>
<td>$d_{13}=0.3$</td>
<td>$d_{15}=2.8$</td>
</tr>
<tr>
<td>(x 10^{-9} esu)</td>
<td>$d_{22}=0.68$</td>
<td>$d_{33}=2.7$</td>
<td>$d_{33}=0.23$</td>
<td>$d_{33}=1.9$</td>
<td>$d_{33}=2.7$</td>
<td>$d_{13}=0.3$</td>
</tr>
<tr>
<td>$d_{32}$</td>
<td>$d_{33}$</td>
<td>$d_{33}$</td>
<td>$d_{33}$</td>
<td>$d_{33}$</td>
<td>$d_{33}$</td>
<td>$d_{33}$</td>
</tr>
<tr>
<td>$d_{eff}$ (pm/V)</td>
<td>0.98</td>
<td>1.65</td>
<td>0.13</td>
<td>NA</td>
<td>NA</td>
<td>0.9</td>
</tr>
<tr>
<td>Damage threshold</td>
<td>13.0</td>
<td>32</td>
<td>40</td>
<td>0.32</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>(GM/cm^2)</td>
<td>(1 n sec)</td>
<td>(32 p sec)</td>
<td>(32 p sec)</td>
<td>(40 n sec)</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

**BTCC**: Bis(thiourea) cadmium chloride;  
**ATCC**: Triallyl thiourea cadmium chloride;  
**ATMB**: Triallyl thiourea mercury bromide;  
**TSCCB**: Thiosemicarbazide cadmium bromide.
2.2. Introduction to renal calculi

Stones – a concentration of material, generally mineral salts, which are formed in an organ or duct of the body are called *calculi* and the formation of calculi is called *lithiasis* [87]. The solid concentrations of dissolved minerals in urine are called *kidney stones* or *renal calculi*. The presence of calculi in the kidneys is called *nephrolithiasis* and the presence of calculi in the urinary tract, which consists of the kidney, ureters, bladder, and urethra (see Figure 2.9), is called *urolithiasis* [88-89]. *Urolithiasis* is one of the most painful disorders and stone formation in the kidney causes a severe amount of pain and suffering to the patient. Acute passage of a kidney stone from the renal pelvis through the ureter results in excruciating pain and discomfort [103].

Figure 2.9: Schematic representations of urinary stone in urinary tract. (Courtesy: http://www.medicinenet.com/kidney).
The primary function of kidneys involves the filtration of metabolites and minerals from the circulatory system. After filtration, the secretions are passed out of the body as urine through the bladder. Some contents of the urine can crystallize and these concentrated chemicals can precipitate into a solid deposit attached to the kidney walls. These crystals can grow through a process of accumulation to form kidney stones. In medical terms, these deposits are called “renal calculi”. In Latin renal means “kidney” and calculi means “pebbles” [88].

Generally, kidney stones contain calcium in combination with either oxalate or phosphate. Uric acid and the amino acid cystine are additional chemical compounds that can form stones in the urinary tract. Also, kidney stone formation can occur due to obstruction of the urine flow or to infection in the urinary tract; the latter types of kidney stones are known as “struvite” or “infection stones”.

Men are more susceptible to develop kidney stones than women, and whites are more vulnerable than blacks. The likelihood of kidney stone occurrence in men begins to rise at about the age 40, and it continues to go up into their 70s. People who have already had more than one kidney stone are prone to develop more stones.

It is believed that renal calculi exist due to mineral supersaturation and crystallization in the urine. Though exact causes of nephrolithiasis are not completely known, some of the current familiar causes are inadequate urinary drainage, existence of foreign bodies in the urinary tract, diet with excess oxalate, calcium, and vitamin irregularity, the use of certain medicines such as diuretics, metabolic diseases such as gout, intestinal dysfunction, cystinuria, etc. In short, kidney stones are formed either due to decrease in urine volume or an excess of stone-forming substances in the urine. The risk of kidney stone formation increases due to dehydration, which can result either from reduced fluid intake or arduous exercise without adequate fluid
replacement. Finally, a family history of kidney stones is also a risk factor for the growth of kidney stones [89-90].

Different conditions that can lead to kidney stones are:

- **Gout**: The amount of uric acid in the urine can increase due to the gout, which, consequently, can lead to the formation of uric acid stones.

- **Hypercalciuria**: A higher amount of calcium in the urine is observed as a result of Hypercalciuria, which is mostly an inherited condition, and is also responsible for stone formation in more than 50 percent of the cases. In this condition, a higher amount of calcium is absorbed from food and excreted into the urine, where it may form calcium phosphate or calcium oxalate stones.

- **Other situations**: There are several other circumstances associated with higher risk of renal calculi such as hyperparathyroidism, kidney diseases (i.e. renal tubular acidosis), and some inherited metabolic conditions like cystinuria and hyperoxaluria. Persistent diseases such as diabetes and hypertension are also associated with higher risk of developing kidney stones. People with inflammatory bowel disease or who have had intestinal bypass surgery are also more prone to nephrolithiasis.

- **Medicines**: Some medicines such as diuretics, antacids with calcium, and the protease inhibitor Crixivan, a drug used to treat HIV infection, can also lead to increased risk of kidney stones.

**2.2.1. Past, present and future of urolithiasis**

Stone formation in the kidney (nephrolithiasis) is one of the oldest and the most common afflictions in humans as well as in animals and birds. Humans have suffered from stones in the
urinary tract (\textit{urolithiasis}) even before the urinary tract was described [91-92]. In short, \textit{nephrolithiasis} and \textit{urolithiasis} have afflicted humans for ages [93].

The history of urolithiasis has begun from the dawn of civilization [94]. The first civilizations developed within fertile areas between 3200 and 1200 BC. The oldest urological object on record is a bladder calculus, which was discovered by \textit{Elliott Smith} in 1901. It was found in a prehistoric Egyptian tomb, in the pelvis of a mummy, and it is dated to 4800 BC. The calculus has a uric acid nucleus with concentric laminations of calcium oxalate and ammonium magnesium phosphate. Urinary calculi also have been found in the graves of North American Indians from 1500-1000 BC. Reference to stone formation is made in early Sanskrit documents in India between 3000 and 2000 BC [93-96].

Even today, people throughout the world, regardless of geographical, cultural, or racial groups, suffer from the \textit{urolithiasis}. In that sense, it is a global problem [97]. The extremely high rate of calculi occurrence in some areas such as the British Isles, Scandinavian countries, northern Australia, Mediterranean countries, central Europe, northern India, Pakistan, and southern states of the United States is so alarming that such regions are known as \textit{“stone belts”} [90,98].

The early incidence of kidney stone formation is estimated to be about 0.5\% in northern America and Europe. In the United States and in other developed countries, the lifetime risk is about 10-15\%, from which about 12 \% of men and 7 \% of women get kidney stone disease at some time. Though urinary calculi are rarely observed among the children of the United States, they are commonly found among the children of Asia [90]. Also, in just over two decades (from the mid-1970s to the mid-1990s), kidney stone occurrence among the citizens of the United States has drastically gone up from 3.2\% to 5.2\% [99-100], and is still rising according to current
Figure 2.10: Number of yearly stone discharges (1997-2002) (Courtesy: C.D.Scales et al. “Changing gender prevalence of stone disease”, J. of Urol. 177, 979-982 (2007))

Figure 2.11: Number of yearly calculi discharges by gender (1997-2002) (Courtesy: C.D.Scales et al. “Changing gender prevalence of stone disease”, J. of Urol. 177, 979-982 (2007)).
research findings. This can be seen from the evidence presented in Figure 2.10 [99]. Moreover, the traditional male predominant calculi prevalence ratio of 3:1 might be changing (see Figure 2.11) [100].

Recently, researchers at the University of Texas at Dallas and University of Texas Southwestern Medical Center identified for the first time the impact of climate change on human health and suggested that because of global warming there may be an increase in the number of cases of kidney stones. These researchers forecasted an increase of up to 30% in kidney stone cases in some areas; specifically for those with elevated temperatures. They predicted approximately 2.2 million new climate-related cases of kidney stones by 2050. If the temperature continues to rise as per their prediction, the fraction of the United States population living in high-risk zones for kidney stones could grow from 40% in 2000 to 56% by 2050 and to 70% by 2095. Moreover, by 2050, the annual health bill of the United States for the treatment of kidney disease could increase by about $1 billion per year, an increase of 25% over the current expenditure [101-102]. Since the amount of money required for the diagnosis and treatment of kidney stones is not trivial, ultimately it results in a financial burden [99]. The cost of treatment includes direct costs as well as indirect costs. The direct costs include evaluation, treatment, hospitalization and professional charges, and indirect costs include lost wages while hospitalized and convalescing. In 1993, in the United States only, approximately US $2 billion were spent for the treatment of patients with kidney stone conditions [104-105].

_Nephrolithiasis_ is mostly an intermittent disease with a relapse rate of 50% in 5-10 years and 75% in 20 years. If it repeats once, then not only is the subsequent relapse risk is increased, but also the gap between recurrences is reduced. Some of the factors connected with recurrence
are: a young age of onset and positive family history of stone infection. Other secondary factors include medical conditions such as hyperparathyroidism [97, 105-107].

In conclusion, though stone formation is an ancient disease, it has not been completely eliminated. Moreover, due to climate change and global warming, the prevalence of kidney stones is increasing throughout the entire world in spite of being studied extensively. Since the exact causes for the kidney stone formation are not completely understood to date, the study of kidney stones retains its importance and relevance.

2.2.3. Composition of urinary calculi

Kidney stones are made of inorganic and organic crystals mixed with proteins. The most commonly occurring stones in human renal calculi are calcium stones, accounting for more than 75% of stones. Most of them are calcium oxalate monohydrate (whewellite) or calcium oxalate dihydrate (weddelite). These crystals can be either pure stones of calcium oxalate or calcium phosphate or a mixture of calcium oxalate and calcium phosphate. Another common type of stones are those comprised of Ammonium Magnesium Phosphate Hexahydrate (AMPH) - MgNH₄PO₄.6H₂O, also called the “struvites”. They are usually seen in the case of urinary tract infections, and, hence, are called “infection stones”. Other compositions are Uric acid, Cystine and Ammonium urate. In general, oxalate, phosphate, uric acid, and urate crystals are the main constituents of urinary calculi. These are summarized in Table 2.4 [92, 97, 108]

2.2.3.1. Struvite or infection stones

Struvite stones, named for the 19th century Russian diplomat Baron von Struv, are also known by other names such as triple phosphate, infection, phosphatic and urease stones as well
as, less commonly, staghorn calculi. Since, the significant stone burden that fills the renal pelvis and calyces forms a shape on radiographs that resembles a deer’s horns (see Figure 2.12), so is it named as staghorn. Staghorn calculus, which involves the entire renal pelvis and calyces, can be composed of calcium oxalate mixed with calcium phosphate.

Table 2.4  Composition of Urinary Calculi (Courtesy: O.W. Moe\textsuperscript{97})

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Percentage of Stone</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Oxalate Monohydrate</td>
<td>40 - 60%</td>
<td>Radio-opaque</td>
</tr>
<tr>
<td>Calcium Oxalate Dihydrate</td>
<td>40 - 60%</td>
<td></td>
</tr>
<tr>
<td>Calcium Phosphate (Apatite; Ca(_{10}[PO_4]_6[OH]_2))</td>
<td>20 - 60%</td>
<td></td>
</tr>
<tr>
<td>Calcium Phosphate (Brushite; CaHPO(_4).2H_2O))</td>
<td>2 - 4%</td>
<td></td>
</tr>
<tr>
<td>Uric Acid</td>
<td>5 - 10%</td>
<td>Radiolucent</td>
</tr>
<tr>
<td>Struvite (Magnesium Ammonium Phosphate)</td>
<td>5 - 15%</td>
<td>Can be staghorn</td>
</tr>
<tr>
<td>Cystine</td>
<td>1.0- 2.5%</td>
<td>Mildly opaque</td>
</tr>
<tr>
<td>Ammonium urate</td>
<td>0.5- 1.0%</td>
<td></td>
</tr>
</tbody>
</table>

Mixed Stones

<table>
<thead>
<tr>
<th>Mixed Stones</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed calcium oxalate – phosphate</td>
<td>35-40%</td>
</tr>
<tr>
<td>Mixed uric acid - calcium oxalate</td>
<td>5%</td>
</tr>
</tbody>
</table>
Staghorn calculus can probably be formed by all other types of urinary stones; however, approximately 75% are composed of a struvite-carbonate-apatite matrix. In western society, most staghorn stones are composed of struvite and can cause significant morbidity and mortality. [109].

*Figure 2.12: Struvite - Staghorn Calculi (Courtesy; eMedicine.com/Struvite).*

Struvite stones are perpetually linked with urinary tract infections. Specifically, the presence of urease-producing bacteria such as Ureaplasma urealyticam and Proteus species, Staphylococcus species, Klebsiella species, Providencia species, and Psedomonas species, leads to the hydrolysis of urea into ammonium and hydroxyl ions [109].

For the formation of Struvite crystals, three conditions are required to occur simultaneously, namely, (1) alkaline urine, (2) the presence of urea or ammonia in the urine, and (3) higher concentration of minerals in the urine. Since struvite forms due to urinary tract infection by urease-producing microorganisms, the urease splits urea and produces ammonia,
followed by the hydrolysis of the ammonia. Due to this hydrolysis, NH$_4^+$ ions are produced, which increases urine pH and produces neutral or alkaline urine. The increased urinary pH not only reduces the solubility of ammonium magnesium phosphate but also favors the precipitation of struvite crystals. Higher ingestion of phosphates (proteins) and magnesium based food as well as less drinking of water increase the level of PO$_4^{3-}$ and Mg$^{2-}$ ions in the supersaturated urine, which leads to the conditions for formation of struvite [92, 109]. Resulting Magnesium Ammonium Phosphate crystals (MgNH$_4$PO$_4$.6H$_2$O) are admixed with carbonate apatite [Ca$_{10}$PO$_4$.6CO$_3$] and hydroxyapatite [Ca$_5$(PO$_4$.CO$_3$.OH)$_3$.OH] in varying proportions along with the matrix [108-110].

The conversions of urea to ammonia, ammonia to ammonium, and acidification from carbon dioxide are as below:

$$H_2NCONH_2 + H_2O \rightarrow 2NH_3 + CO_2$$ \hspace{1cm} (10)

$$2NH_3 + H_2O \rightarrow 2NH_4^+ + 2OH^- \quad \text{(Increased pH>7.2)}$$ \hspace{1cm} (11)

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-}$$ \hspace{1cm} (12)

Though the urine of a healthy person is not supersaturated, the precipitation of struvite can take place due to a condition aggravated by urease-producing microorganisms and the urine’s multifaceted composition. In such circumstances struvite frequently precipitates collectively with apatites and the residue can easily be attached to particles of organic matter formed as a result of infection. Since this mechanism favors the crystal deposition and accumulation, struvite grows rapidly. Struvite may grow speedily within a short period of time, and if not sufficiently treated, can build up Staghorn calculus [92]. If struvites are not treated
sufficiently, there is evidence that struvites can lead to an increased risk of renal loss, sepsis, and death [111]

2.2.4. Importance of traditional approach to nephrolithiasis

The occurrence of urinary stones, unlike other human diseases, was recognized far back in ancient times [91-93]. Among the different types of stones that can occur in urolithiasis, some of the most common types are calcium oxalates, struvites, etc. In the formation of these crystals, there are several physiochemical phenomena involved, such as crystal nucleation, growth and aggregation, ending with retention within the urinary tract. The mechanisms governing the initiation of all of these processes are not completely understood. Moreover, one of the most important characterizing phenomena of urolithiasis is its high rate of recurrence. So, it is extremely important to have appropriate management for urolithiasis treatment. Unfortunately, such treatments are not just expensive but in most cases they are debilitating and cause side effects. Therefore, it is quite important and a worthy endeavor to search for an alternative to such approaches, such as, for example, the use of medicinal plants [111].

Hence, medical practitioners and patients are significantly interested in the identification of efficient measures for promoting stone passage, stone dissolution, and stone prevention. So, it is extremely important to evaluate the roles of not only conventional Western rehabilitation but also conventional complementary remedies like Ayurvedic medicine [112].

2.2.4.1. ‘Ayurveda’- Indian traditional curative system in urolithiasis

Ayurveda is a Sanskrit word and it stands for “the knowledge of life span” and it is considered the most antique existing curative system. It was originated in India more than 3,000
years ago. It is the healing method which includes herbal, mineral and animal therapies, dietary modification, meditation, yoga, aroma therapy, and music therapy [112]

Ayurveda is a comprehensive natural health care system, still widely used in India as a primary health care system. Additionally, the interest in it is growing throughout the world [113]. Ayurveda gained appreciation in the Western world because medical researchers and scholars outlined its different postulates. Research has been conducted worldwide on Ayurveda. In the United States of America, NIH (National Institute of Health) spends some of its $123 million budget on Ayurvedic medicine research [114]. Ayurveda has unique concepts and methodologies for dealing with health care completely during the course of life, from pregnancy and infant care to geriatric disorders.

2.2.4.2. Rotula Aquatica Lour

The “Pashanbheda” group of plants considered to be useful in the treatment of urinary stones. In the Ayurvedic system of medicine, the word “Pashanbheda” is used for a group of plants having diurectic and antiurolithiatic activities. Pashanbheda” is the Sanskrit word; in it, which “Pashana” represents stone and Bheda” indicates break [115]. Among various pashanbheda plants, Rotula Aquatica Lour is also one of the important “Pashanbheda” plants and is known for antiurolithiatic activity.

Rotula Aquatica Lour is a botanical name and it is a member of the “Boraginaceae” family. In Sanskrit, an ancient Indian language, Rotula Aquatica Lour is known as “Pashanabhedah”, “Asmabheda” and “Mootrala”. In Hindi, the Indian National Language, it is called “Pashanbhed” [116]. Rotula Aquatical Lour has been used as a remedy for the
treatment of piles, diabetes, renal, and venereal disease and urolithiasis in conventional Indian medicine.

The effect of the Rotula Aquatica Lour plant, on renal histopathology, urinary composition and serum electrolytes was observed during an animal study. In a rat model of calcium oxalate urolithiasis, Rotula Aquatica Lour also caused a reduction in calcium and oxalate levels and it also prevented histopathologic abnormalities noted in the untreated animals: dilated tubules, microcrystals and epithelial cell damage. However, no significant change was noted in serum calcium, phosphate, or magnesium [112]
CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1. Crystal Growth

The advances in solid state science depend critically upon the availability of single crystals. As a consequence, an enormous amount of effort and care has been directed towards on the development of growth techniques. Talking in terms of crystal sizes, purities and perfections, the achievements of the modern crystal growers are indeed noteworthy and appreciable, as huge sections of industry now rely on these products.

Many new materials have already been grown as single crystals. Some of them are relatively easy to obtain, such as ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP), silicon, germanium, etc. Others, such as hydroxyacetate, cholesterol, protein and most biomaterial crystals are only synthesized by a long, arduous growth process. Also, there are still many other substances which have not yet been grown in single crystal forms, e.g. iron tartrate crystals, and others which have never been obtained in the required size and degree of perfection, such as lanthanum tartrate, neodymium tartrate, promethium tartrate and several other rare earth tartrate crystals. All of these compounds present a challenge and an opportunity to the professional crystal growers. Many times, crystal growing is known as an art as well as a science, because a lot of care is required to attain good quality single crystals. In confirmation of this are Gilman’s remarks in his book “Art and Science of Growing Crystals” [117], which are noteworthy and are quoted as follows:
“The systematic production of artificial crystals might be viewed as a new ‘agriculture’ that has begun to flourish. This new agriculture consists of ‘growing’ solid crystals from a ‘nutrient’ phase. (gas, liquid or solid). To start the process, the nutrient is often ‘seeded’ with small pieces of crystals to be grown and some workers speak of ‘reaping the harvest’ after a certain length of time’.

There is abundant literature that describes in detail different crystal growth techniques [117-120]. A schematic classification of most frequently employed growth methods is provided below, as presented by Laudiese [121]:

I MONOCOMPONENT:

(A) Solid –Liquid (recrystallization)

1. Strain-annealing
2. Devitrification
3. Polymorphic phase change
4. Sintering

(B) Liquid- Solid

1. Conservative
   (a) Directional Solidification (Stockbarger- Bridgeman)
   (b) Cooled Seed (Kyropoules)
   (c) Pulling (Czochralski)
2. Non –Conservative
   (a) Zoning (horizontal, vertical, float-zone, and growth on pedestal)
   (b) Vernuil (flame fusion, plasma, and arc image)

(C) Gas- Solid
1. Sublimation – Condensation

II POLYCOMPONENT:

(A) Solid – Solid

1. Precipitation from solid solution (exsolution)

(B) Liquid – Solid

1. Growth from solution (evaporation, slow cooling, and zone melting)
   
   (a) Aqueous Solvents
   
   (b) Organic Solvents
   
   (c) Molten Salt Solvents
   
   (d) Solvents Under Hydrothermal Conditions
   
   (e) Other Solvents (Metals)

2. Growth by reaction (temperature change, concentration change)

   (a) Chemical Reaction
   
   (b) Electro Chemical Reaction

(C) Liquid – Solid

1. Growth by reaction (temperature change, concentration change)

   (a) Van Arkel
   
   (b) Epitaxial

   (c) Gas Phase growth of inorganic

(D) Composite (Vapor- Liquid- Solid)

Laudiese [121] did not include gel growth in this classification; however, gel growth falls into the category of solution growth techniques.
3.1.1 Comparison of Different Growth Techniques

These growth techniques have their own respective advantages as well as disadvantages. For example, the monocomponent methods based on liquid-solid equilibrium are more rapid than the polycomponent techniques, because they do not involve diffusion to any appreciable extent. The dissipation of the heat of fusion is the limiting step for this consideration. However, for crystallization at a reduced temperature, either the polycomponent method or the solid-solid monocomponent techniques must be used. On the other hand, the solid-solid techniques impose severe problems of nucleation control since in the solid undergoing transition to the desired phase, the nuclei density is orders of magnitude higher than in more attenuated systems. Also, besides the diffusion issue, the polycomponent methods exhibit the problem of second component solubility in the grown crystal. Therefore, the growers have to compromise between the growth rate and the purity to achieve crystallization at low temperatures.

Several possible solid-solid transformation techniques have yet to be exploited. For example, the apparent difficulties of the growth processes by controlled devitrification or exsolution need to be reconsidered. Not enough care has been employed in the limiting case of nucleation in solid-solid transformation. Also, growth by strain annealing has been almost entirely limited to metals and a few nonmetals that can support high strains short of rupture.

The most useful of all the crystal growth methods is by liquid-solid, since it combines speed with easy observation of potential modifications during the growth process. The various modifications mainly include details of the geometry of the liquid-solid interface and the way it moves through the melt. Also, it does not require determination of phase equilibrium and solubility relationships, as do other methods.
Other techniques such as molten salt and hydrothermal growth require extensive knowledge of the systems under study. Therefore, preparation of large crystals in preliminary stages cannot be easily used in these methods. On the other hand, because crystal pulling can be employed on these systems without any prior knowledge of the phase relationship, this approach is mainly used for searching for new piezoelectric, ferroelectric, laser modulator and harmonic generator materials. The most used technique is the sealed Stockbarger-Bridgman.

Either liquid-solid or gas-solid polycomponent methods are mostly employed for low temperature growth processes. It is easier in expitaxial vapor growth to obtain sharp concentration gradients and to control the layer thickness. However, vapor growth is perhaps not as attractive for growing bulk crystals as is the solution method, which presents more flexibility.

Since a large thermal gradient can be easily obtained in the zone melting technique, numerous semiconductors and other types of materials have been synthesized by this method [122-123]. Finally, among other polycomponent methods we shall consider the recent revival of interest in gel media growth. Henisch, Dennis and Hanoka have achieved considerable success in growing lead iodide, and sodium, calcium and strontium tartrates and sodium oxalate by this last mentioned method. The gel growth method is described in detail in section 3.3.

### 3.2 Aqueous Solution Growth Techniques

In this technique supersaturation is obtained without inducing spontaneous nucleation so that growth can proceed on the seed material. Depending on the desired results, this supersaturation can be achieved and maintained in different ways such as:

- The water can be evaporated
- The solution temperature can be deceased
Solution, saturated at a temperature higher than the growth temperature, can be continuously introduced into the growth chamber.

A general schematic of a crystallizer used in the aqueous solution growth technique is shown in Figure 3.1.

3.2.1 Crystal Growth by Slow Evaporation of the Solvent

This is the simplest technique and it is quite suitable for growth of substances that are moderately soluble at room temperature, and which are either not much more soluble or are unstable at higher temperatures. In this method, a near saturated solution is prepared by using a suitable solvent. Then, the sample can be left in a sample vessel that has a perforated cap. The
perforation size is an experimental variable, which relies to some extent on the volatility of the sample. In order to facilitate the effortless exclusion of the fragile crystals, it is advantageous to incline the tube so that some of the crystals grow on the side of the tube. It is imperative to harvest the crystals before all of the solvent has evaporated [124-125].

3.2.2 Crystal Growth by Slow Cooling of the Solvent.

This technique is good for solute-solvent systems, which are less than moderately soluble, and in which the solvent's boiling point is less than 100 °C. In this method, a saturated solution of the compound is prepared, where the solvent is heated to just its boiling point or to a few degrees below it. The solution is allowed to cool down slowly. Sometimes, turning off the heat and letting the solution slowly cool on the hot plate (without stirring) works well. However, if the solution cools very rapidly because of the low temperature of the surroundings, the sample container should be insulated. Although, commercial ovens are available, a Styrofoam cup or packing base from acid bottles covered with metal foil may work as well to slow the rate of cooling [124-125].

3.2.3 Sample Preparation for L-arginine Doped KDP Crystals

Due to good solubility in water of the parent material KDP as well as of the dopant amino acid, the slow evaporation technique was employed in growing the crystals for the current work [126]. This technique has been described abundantly in literature [126-136]. The doping of KDP crystals with L-arginine was achieved by adding 0.3, 0.4, and 0.5 wt% solution into the saturated KDP solution. The mixture was thoroughly stirred for 8 h for homogenization.
The solubility curve of KDP in double distilled water was measured by means of conventional weight analysis and it was compared and confirmed with the literature value reported by Yang Shangfeng et al [136]. The solubility study of pure KDP in water was studied for different temperatures. For this, a 250 ml glass beaker covered with a rubber cork was kept on a platform in a constant temperature bath, with an accuracy of 0.1 °C. After achieving saturation, the content of the solution was analyzed gravimetrically. The amount of KDP dissolved in 100 ml of water was plotted as a function of temperature.

3.2.3.1 Preparation of seed crystals.

At room temperature, the slow evaporation of the solvent leads to supersaturation. When supersaturation is reached, crystal nucleation starts. Thus, after comparing the solubility data, the saturated solution of KDP was prepared at 40°C by constant stirring for 8 hours. The solution was kept inside a preheated oven (40°C) to achieve homogeneity. Then, it was filtered in a beaker and poured equally into four Petri dishes, each of which was closed by a perforated cover to allow water evaporation. In three Petri dishes, 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine concentrations were added. The solutions were well stirred till a complete dissolution of L-arginine was achieved. The remaining forth Petri dish, containing the mother solution, was used as a standard. The resulting seed crystals were then harvested using single thread of nylon.

3.2.3.2 Preparation of larger sizes of pure and L-arginine doped KDP single crystals.

The best quality seed crystals were selected and placed at the bottom of four beakers containing the appropriate solutions for growth. The pure and L-arginine doped KDP solutions were prepared as previously described. The beakers were again closed with perforated covers and kept in a constant temperature bath at 40°C to allow the slow evaporation of the solvent. As the solvent evaporates the excess of the solute deposits on the seed crystals and allows the
formation of larger crystals. The pure and L-arginine doped KDP crystals were harvested after a period of 8-10 days. A schematic design of the system employed in the growth process is presented in Figure 3.2

Figure 3.2: Crystal growth set-up for slow evaporation and slow cooling technique

Direct evidence of the quality of the resulting and further analyzed crystals is presented in Figure 3.3 (a) to (d) for the standard KDP crystals and for the 0.3, 0.4 and 0.5 wt.% L-arginine doped KDP.
Figure 3.3: Illustrations of: (a) pure KDP crystals; (b) 0.3 wt.% L–arginine doped KDP crystal; (c) 0.4 wt.% L–arginine doped KDP crystal; and (d) 0.5 wt.% L–arginine doped KDP crystal.
3.3 Gel Growth Technique

3.3.1 Brief History of Gel Growth

The subject of crystal growth in gels is not new. Indeed, it has already enjoyed at least two long periods of popularity. One during the second half of the nineteenth century, and one roughly during the period 1923-1926 when famous “Lisegang Rings” formed the main subject of interest, e.g., the work of authors like Lisegang [137], Bradford [138] and Holmes [139]. These intriguing and often beautiful periodic structures are frequently observed in nature and easily reproduced in the laboratory.

Larger crystals several mm in size were occasionally obtained but not systematically pursued. In contrast, the growth of such crystals is the principal objective of all modern work in this field. According to Fisher and Simons [140], “gels form excellent media for the growth of crystals of almost any substance under absolutely controllable conditions”.

Experiments during the early period derived a good deal of impetus from the interests of geologists, who believed that all quartz on earth was at one time a silica hydrogel. Moreover, some early experiments were on record, quoted by Eitel [141], according to whom microscopic silica crystals had been obtained from silica gels in the presence of various “crystallizing agents” when heated under water vapor pressure. Quite plausibly then, crystalline foreign deposits found in quartz may be examples of crystal growth in gel. In this way, the gel method appeared to offer systems and opportunities for experiments in “instant geology” [142].

Among the earlier workers, Hatschek [143] worked primarily with (5-20%) gelatin and (1-5%) agar gels. He was the first to make a systematic study of particle size distribution in a great variety of Liesegang rings. It was always realized that reagents could be diffused into a gel and conversely, that gel could be dialyzed to free them of excess reagents or unwanted reaction
products. The experiments were conducted by Holmes [144], who used the dialyzing process for
the treatment of gel in U-tubes in order to eliminate excess reagents, which might interfere with
the two diffusing components. Holmes also grew single crystals of copper and gold by diffusing
a reducing agent into gels charged with the appropriate salts.

Later on, Henisch et al. [145] described a method for growing single crystals from silica
gels. Also Henisch [146] explained all aspects of the gel growth techniques in detail.

### 3.3.2 Gelling Mechanism

The gelling process can be bought about in many ways, sometimes by the cooling of a
sol, by chemical reaction, or by the addition of precipitating agents. Gelatin is a good example of
a substance which is readily soluble in hot water and can be gelled by cooling provided that the
concentration exceeds about 10%. Formation of gel can be obtained by the reaction of two
reagents in concentrated solution; preparation of silica gel is an example of this.

The process of gelling takes an amount of time that can vary widely from minutes to
many days, depending on the nature of the material and its temperature [146]. This has been
described and documented by Treadwell and Wieland [147] for silica gel. Also, mechanical
properties of fully set gels can vary widely, depending on the density and on the precise
conditions during gelling. For diffusion of reagents through the gel medium, the most important
operative parameter is the size of the diffusing particle relative to the pore size in the gel.
Another important parameter is the amount of substance absorbed on silica hydrogel [148]
Comparative merits and demerits of various gels used for crystal growth are given by Patel and
Rao [149].
3.3.3 Structure of Silica Hydrogel

Silicon hydrogel is the most favored gel for crystal growth experiments. Hence, the study of its gelling mechanisms and gel structure carries considerable importance. When sodium metasilicate goes into solution, monosilicic acid is produced in accordance with the dynamic equilibrium

\[
Na_2SiO_3 + 3H_2O \rightarrow H_4SiO_4 + 2NaOH \quad (3.1)
\]

The monosilicic acid can polymerize with the liberation of water.

This can occur repeatedly until a three dimensional network of Si-O links is established as in silica.
As the polymerization process continues, water accumulates on top of the gel surface. This phenomenon is known as “syneresis”.

The time required for gelation is very sensitive to pH. At very low pH values, the tendency towards polymerization is diminished and chain formation is slowed down. Gelation time strongly depends on temperature [150]. This has been described in detail by Henisch [146].

A weak acid is generally preferred to adjust the pH, because the pH of the set gel changes slightly with time, and secondly, the mineral acids tend more or less to spoil the growing crystal. It is noteworthy that in less acidic gel solutions the reaction between the acid and sodium metasilicate occurs with liberation of hydrogel ions and thus the pH of the solution rapidly increases with the process of polymerization, while in highly acidic gel there is no change in pH except due to very small differences in dissociation of acids of different complexities. Hence, pH has profound influence on the gel structure [151].
### 3.3.4 Gel Growth Methods

Crystal growth in gel has been mainly divided into the following five different methods.

1. Reaction Method
2. Chemical Reduction Method
3. Complex Decomplexion Method
4. Solubility Reduction Method
5. Electrolytic Method

#### 3.3.4.1 Crystal Growth by Reaction

This method is the basis of all methods of gel growth and can be described as crystal growth by chemical reaction.

Two aqueous solutions of soluble salts, suitably chosen are allowed to come together by diffusion through the gel so that there can be a slow and controlled segregation of ions and molecules resulting in the precipitation of an insoluble phase as the crystal. The gel method is to limit the number of critically sized nuclei and decrease the rate of crystal growth either by controlling the diffusion of reacting ions or by governing the reaction velocity on the surface of the growing crystal. The resulting chemical reaction can be expressed as,

\[ AX + BY \rightarrow AY + BX \]  

(3.2)

where, A and B are the cations, X and Y are anions.

In this method two soluble reactants are allowed to diffuse through the gel, where they react and form an insoluble and relatively less soluble crystalline product. This can be done by
the test tube technique, in which one of the reactants is incorporated in the gel and the other reactant is diffused into it as shown in Figure 3.4, or by the U-tube technique, Figure 3.5, in which the two reactants are allowed to react by diffusion into an essentially inactive gel. There is a variety of crystallization apparatus employed to grow single crystals by these methods. The disadvantage of the first crystallization apparatus is the depletion of one of the reactants, which is one inside the gel.

Figure 3.4: Test tube technique

Figure 3.5: U-tube technique
Since these crystallization apparatus exhibit certain limitations such as the depletion of one of the reactants (which is inside the gel), an improved design of the modified gel growth technique used by Patel and Rao [149] is depicted in Figure 3.6. This technique eliminates all the inconveniences of the previous gel growth techniques and it permits the growth of mixed and doped crystals by multiple diffusions.

![Figure 3.6: Modified gel growth technique.](image)

3.3.4.2 Chemical Reduction Method

This method is suitable for growing only metal crystals from gel media. Hatschek and Simons [152] were the first to report the growth of gold crystals by adding 8% oxalic acid solution over a set gel containing gold chloride solution. Several metallic crystals such as gold, lead, copper, etc. have been grown by this method.
3.3.4.3 Complex-Decomplexion Method

This method consists of first forming a chemical complex of the material of the crystals to be grown with an aqueous solution of some suitable substance, called the complexing agent, in which the former is homogeneously mixable, and then providing, externally, a condition conductive to decomplexing. A standard procedure adopted for decomplexion is to increase the dilution steadily, while the complex solution is diffused through the gel. Crystal growth by this method was first attempted by O’Connor et al. [153] for the growth of cupric halide crystals.

3.3.4.4 Solubility Reduction Method

This method is applicable for growing single crystals of highly water soluble substances. In this method, the substance to be grown is dissolved in water and is incorporated with the gel forming solution. Then a solution which reduces the solubility of the substance is added over the set gel to induce crystallization as in Figure 3.7. For instance, potassium dihydrogen phosphate (KDP) crystals have been grown by adding ethyl alcohol over the gel containing a saturated solution of KDP [154]. Crystals are grown due to reduction of solubility of KDP in the liquid phase by the diffusing alcohol.

3.3.4.5 Electrolytic Method

This electrolytic method can also be used for the growth of metallic crystals by using the gel medium for controlled growth. For this a very low D.C. electric current, usually of the order of 2-10 mA, is passed through a silica gel charged with suitable acid or electrolytic solution, as shown in Figure 3.8. It has been observed that the pH of the gel medium, the concentration of the
supernatant solution, the current density and the materials used as electrodes, have had considerable influence on the habit of the crystals grown.

Figure 3.7: Experimental set-up for solubility reduction method.

Figure 3.8: Experimental set-up for electrolytic method.
3.3.5 Simple Model for In Vitro Study

By and large, the standard laws of physical chemistry are helpful for providing the explanation for the growth of crystals in a static solution, but in the case of human urine, the situation is totally different. Since fresh solutes are added to and removed from this solution, normal human urine is not a static solution. Hence, it is difficult to mimic the urinary tract in \textit{vitro}. However, since the growth of crystals in gel media occurs under static conditions, this helps to explain the growth of urinary calculi in the body to a certain level. The silica hydrogel is frequently used as the medium for the growth of the crystals. In order to make the gel, sodium meta-silicate (Na$_2$SiO$_3$) of desired specific gravity is mixed with diluted acid; the use of diluted acid helps to obtain a suitable pH value. The mixture produces monosalicylic acid, which polymerizes with liberation of water. This process repeats itself and a three-dimensional network of Si-O links is created. The pores in the gel are separated by a solid film of $2\times10^{-5}$ cm thickness, and the dimensions of the pores depend on the concentration of the gel. The effective pore diameter of silica gel is of the order of 50-100 Å [155].

As a result of the diffusion of two different types of reactants, a critical concentration occurs at certain places in the gel and a few nuclei are produced. Additionally, the supply of nutrients to the nuclei helps them to grow into the crystal. Typically glass test tubes or U-shaped tubes are chosen as crystallization apparatus [145, 146, and 149]. The gel framework is chemically inert and it acts like a three-dimensional matrix or a container in which the crystal nuclei are delicately held and supplied with different nutrients for growth. This method can be considered as a straight-forward model for studying the growth of urinary calculi in the human body under \textit{in vitro} conditions [155].
3.3.6 Sample Preparation for pure and Rotula Aquatica Lour (RAL) incorporated struvite crystals

The complexity of calculi formation (i.e. nucleation, transformation, and aggregation) in a natural system such as urine is simulated to a certain extent in this work by using a simplified single diffusion gel growth technique. The ammonium magnesium phosphate hydrate crystals were synthesized in a static gel environment without and with the presence of RAL herbal extracts as follows: a sodium metasilicate solution of specific gravity 1.05 and an aqueous solution of ammonium dihydrogen phosphate of 0.5 M concentration were mixed at a set pH value of 7.0. Equal amounts of supernatant solutions of 1.0 M magnesium acetate prepared with 1% and 2% concentrations of the herbal extract of RAL were gently poured on the set gels in the respective test tubes in the aseptic medium [156]. The apparent lengths of growing / dissolving crystals in each of the test tubes, without and with herbal extracts were measured at regular time intervals [156]. The grown crystals are shown in Figure 3.9.

![Figure 3.9](image)

**Figure 3.9:** (a) Pure struvite crystal (Bigger and White), (b) 1 wt% and (c) 2 wt% Rotula Aquatica Lour incorporated struvite (decreased size and change in color) crystals
3.4 Thermogravimetry

Thermogravimetry (TG) provides the analyst with a quantitative measurement of any weight change associated with a transition. For example, TG can directly record the loss in weight with time or temperature due to dehydration or decomposition. Thermogravimetric curves are characteristic for a given compound or system because of the unique sequence of physicochemical reaction occurring over definite temperature ranges, at rates that are functions of the molecular structure. The changes in weights are results of the rupture and/or formation of various physical and chemical bonds at elevated temperatures, which consequently lead to the evolution of volatile products or the formation of heavier reaction products [157].

In the present investigation the thermogravimetric analysis on powdered samples were carried out on a TA Instruments SDT 2960 Simultaneous DTA-TGA (see Figure 3.10) from 30 °C to 900 °C in an atmosphere of air and at the heating rate of 10°C/min. Weight calibration was performed using ceramic and platinum crucibles. The temperature calibration was done with In (m.p. 156.2 °C), Zn (m.p. 418.4 °C) and Al (m.p. 658.3 °C) metals.

Figure 3.10: (a) Experimental set-ups for Thermo Gravimetric Analysis (TGA)
Figure 3.10: (b) Complete view of experimental set-ups for Thermo Gravimetric Analysis

3.5 Fourier Transform Infrared (FT-IR) Spectroscopy

*Fourier Transform Infrared* (FT-IR) spectroscopy is a characterization technique that provides information about the chemical bonding, or indirectly, about the molecular structure of organic as well as inorganic materials. With the help of this technique, it is possible to identify unknown materials present in a specimen.

The technique is based on the characteristic frequency vibrations of the chemical bonds or a group of chemical bonds in a material. This is because a molecule exposed during FT-IR analysis to a modulated infrared beam absorbs energy at frequencies which are characteristic of that molecule. For a typical specimen, the absorption or the transmission of the infrared rays at different frequencies is translated into a plot consisting of peaks or dips, respectively. The outcome of the FT-IR spectrum is then analyzed and matched with known signatures of already identified materials and collected in FT-IR libraries. In order to perform FT-IR analysis, small quantities of material, whether solid, liquid or gaseous, are required. When an FT-IR library does
not provide an acceptable match, individual peaks in the FT-IR plot may be used to yield partial information about the specimen [158].

The spectra collected based on this technique are measurements of the temporal coherence of a radiative source (using time-domain measurements) of electromagnetic radiation or of some other type of radiation. There are several methods for measuring the temporal coherence of light, such as the continuous wave Michelson spectrometer, also called the Fourier transform spectrometer, and the pulsed Fourier transform spectrograph.

The Fourier transform spectrometer is nothing but a Michelson spectrometer with a movable mirror, which relies on the same principle as the Michelson Morley experiment and is schematically presented in Figure 3.11.

![Figure 3.11: Scheme of Michelson spectrometer.](image-url)
The light from the source is splitted into two beams by a half silvered mirror. One beam is reflected off a fixed mirror and one off a moving mirror, which introduces a time delay. The beams interfere, allowing the temporal coherence of the light to be measured at each different time delay setting. By making measurements of the signal at many discrete positions of the moving mirror, the spectrum can be reconstructed using a Fourier transform of the temporal coherence of the light. This type of interferometer is capable of very high spectral resolution observations of very bright sources [159].

The detected intensity as a function of moving mirror position, I(x), can therefore be converted into the intensity spectrum as a function of frequency, G(k), by a simple Fourier transform.

\[ W(x) = \frac{2I(x) - I(0)}{\sqrt{2\pi}} = \frac{1}{\sqrt{2\pi}} \int G(k) e^{ikx} dk \]  

(3.3)

3.6. Raman Spectroscopy

Nowadays, Raman spectroscopy is an important analytical and research technique since information about chemical and molecular structure, as well as the stress on a sample can be easily acquired. It can be used to analyze different types of samples such as polymers, thin films, semiconductors, pharmaceuticals, fullerenes, and other carbon nanomaterials.

Raman spectroscopy, a light scattering technique, is a process where a photon of light interacts with the sample surface to produce scattered radiation at different wavelengths. This technique is based on the Raman-effect, which was discovered by the Indian physicist C.V. Raman in 1928. Although it is defined as an inelastic scattering process of photons by molecules, the Raman scattering comprises a very small fraction of about 1 in $10^7$ of the incident photons.
Though this type of scattering was demonstrated in 1928 by professor C.V. Raman, Raman spectroscopy was not popular until 1990 as compared to other characterization techniques such as *Fourier Transform Infrared Spectroscopy*, *Ultraviolet-Visible Spectroscopy*, and *Nuclear Magnetic Resonance Spectroscopy*. The Raman revolution started with the new generation of smaller, compact instruments that utilize newer lasers, optics and detectors [160].

### 3.6.1 The theory of Raman spectroscopy

When monochromatic radiation is incident upon a sample, it may be reflected, absorbed or scattered in some manner. Among all these phenomena only the scattering process is important in Raman spectroscopy, since it provides information about the molecular bonding of the sample.

As the photons interact with molecules they induce transitions between energy states. Thus, the scattered radiation does not contain only the incident frequency, but can also contain a small amount of radiation scattered at a different frequency as shown in Figure 3.12.

![Figure 3.12: Inelastic and elastic scattering of photon from a molecule.](courtesy of Horiba-Jobin Yvon)

If the scattered light does not exhibit a change in frequency, and hence, in wavelength, then the scattering process is called *elastic* or *Rayleigh scattering* (this process was described by
Most photons are elastically scattered. Only a very small part, approximately $1 \times 10^{-7}$ of the scattered light, exhibits a change in frequency, a process called **Raman or inelastic scattering**. It is the change in wavelength of the scattered photon which provides the chemical and structural information.

Thus, depending upon the vibrational state of the molecule, the Raman shifted photon can possess either higher or lower energy. This can be easily understood from a classical explanation point of view of the Raman effect which is due to the interaction of the electromagnetic field of the incident radiation, $E_i$, with a molecule. The electric field may induce an electric dipole in the molecule which can be expressed as:

$$P = \alpha E_i \quad (3.4)$$

Where, $\alpha$ is the polarizability of the molecule and $P$ is the induced dipole.

Since the electric field due to the incident radiation is a time-dependent quantity given by:

$$E_i = E_0 \cos(2\pi \nu_i t) \quad (3.5)$$

for a vibrating molecule, the polarizability is also a time varying term. Its dependence on the vibrational frequency of the molecule, $\nu_{\text{vib}}$, is:

$$\alpha = \alpha_0 + \alpha_{\text{vib}} \cos(2\pi \nu_{\text{vib}} t) \quad (3.6)$$

Multiplying the two time-varying terms $E_i$ and $\alpha - \alpha_0$ we obtain:

$$\frac{\alpha_{\text{vib}} E_0}{2} \left[ \cos 2\pi (\nu_i + \nu_{\text{vib}}) + \cos 2\pi (\nu_i - \nu_{\text{vib}}) \right] \quad (3.7)$$

This cross term in the induced dipole indicates that the light can be scattered at higher energy as well as lower energy than the Rayleigh scattering of the incident radiation. The incremental differences to the frequency of the incident radiation ($\nu_i$) are the vibrational
frequencies of the molecule ($v_{\text{vib}}$). If the scattered photon has a higher frequency (energy) than the incident photon, the scattering is called **anti-Stokes Raman scattering**, and if it has a lower frequency (energy) is called **Stokes Raman scattering**.

The Rayleigh, Stokes, and anti-Stokes Raman scatter components are presented in Figure 3.13. In molecular systems, these frequencies are in energetic ranges associated with rotational, vibrational and electronic level transitions. The scattered radiation occurs in all directions and may also have observable polarization changes with wavelength [161].

![Figure 3.13: Schematic representation of: (a) Stokes Raman scattering, (b) Rayleigh scattering, and (c) Anti-Stokes Raman scattering.](image)

At room temperature the population state of a molecule is principally in its vibrational ground state. A small number of molecules will be at a higher vibrational level. Therefore, the Stokes scattering process is much stronger than the anti-Stokes one. In Stokes scattering, the photon is shifted towards the red end of the spectrum (has lower energy or larger wavelength). In
contrast, a blue wavelength shift is observed for the scattered photon in an anti-Stokes process (has higher energy or smaller wavelength).

The energy increase or decrease from the excitation is related to the vibrational energy spacing in the electronic states of the molecule. Therefore, the wavenumbers of the Stokes and anti-Stokes lines are measures of the vibrational energies of the molecule. Also, as can be depicted in Figure 3.14, the Stokes and the anti-Stokes lines are situated at equal frequency differences from the Rayleigh line. This happens because in either case one vibrational quantum of energy is gained or lost. Since only a molecule excited prior to the irradiation can give rise to the anti-Stokes line, it could be also observed in Figure 3.14 that this line is less intense than the Stokes line. So, in Raman spectroscopy generally, the more intense Stokes lines are measured.

![Figure 3.14: Schematic representation of Rayleigh, Stokes and Anti-Stokes lines.](image)

The amount of energy change of a photon in its interaction with a molecule is characteristic of the nature of each chemical bond. Though it would not be possible to observe all
vibrations through Raman spectroscopy, more than enough information can be obtained to perform a very precise characterization of the molecular structure.

3.7. Comparison of Infrared Absorption and Raman Spectroscopy

Infrared absorption and Raman spectroscopies both measure the vibrational energies of molecules. However, these methods rely on different selection rules; they are complimentary techniques. For a vibrational motion to be infrared active, the dipole moment of the molecule must change. For example, as can be observed in Figure 3.15, the symmetric stretch in carbon dioxide is not infrared active because there is no change in the dipole moment, but the asymmetric stretch is infrared active since it is due to a change in dipole moment. On the other hand, in order to be a Raman active transition, a change in polarizability of the molecule is necessary, as can be seen in Figure 3.16 for the symmetric stretching mode of CO$_2$.

![Figure 3.15](image)

Figure 3.15: The dipole moment for symmetric and asymmetric stretch in CO$_2$.

![Figure 3.16](image)

Figure 3.16: The polarization for different vibrational motions of CO$_2$ molecule.
For example, homonuclear diatomic molecules do not exhibit a change in the dipole moment; therefore, they have a featureless infrared absorption spectrum. However, because stretching and contraction of the bonds change the interactions between electrons and nuclei, and hence, change the molecular polarizability, they do have a Raman spectrum. For highly symmetric polyatomic molecules possessing a center of inversion (such as benzene) it is observed that bands that are infrared active are not Raman active. Molecules with little or no symmetry are likely to be both infrared and Raman active [162-163].

### 3.8 Bruker IFS66v FT-IR Spectrometer

The commercial rapid-scan vacuum based *Brucker IFS 66v Fourier Transform infrared interferometer* with various upgrades was used to characterize the pure and the 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped KDP crystals. The vacuum facility of this system allows experiments in the far-infrared region, where atmospheric absorption becomes dominant.

The system and the scheme of its internal optics beam path are shown in Figure 3.17 and Figure 3.18, respectively. Figure 3.18 is useful to understand how the Bruker IFS 66v FT-IR and the FRA 106/S FT-Raman module work.

*Figure 3.17: Bruker IFS 66v FT-IR spectrometer (courtesy Bruker Inc.).*
Figure 3.18: Optical diagram of the Bruker IFS66v FT-IR spectrometer and of the Bruker FRA106 FT-Raman system (courtesy Bruker Inc.).

The beam sent from the IR source to a parabolic mirror is focused on an aperture changer. After the beam passes through the iris, a concave mirror deviates it by 90 degrees. At this point, we have exactly a Michelson interferometer, as previously described. The beamsplitter divides the beam in two. The beam which crosses the beamsplitter in the straight direction goes to a movable mirror, which reflects it back to the beamsplitter. The second part of the collimated beam is again reflected back to the beamsplitter by a fixed mirror. The electromagnetic wave resulting from the recombined light at the beamsplitter can interfere in two different ways: constructively and destructively. The interference depends on the optical path difference and on the wavelength of the light. The relationship is as follows:

1. Constructive interference  \[ 2\delta x = n\lambda \quad n = 1, 2, 3\ldots \]
2. Destructive interference  \[ 2\delta x = (1/2) n\lambda \quad n = 1, 3, 5\ldots \]
Consequently, the output beam has an intensity that varies as a function of the optical path difference and the wavelength of the incident radiation. The intensity is at a maximum when the optical path difference is zero, since light of all wavelengths constructively interferes at this point called the zero path difference (ZPD).

A common procedure is to allow the movement of the mirror at a constant velocity, so that the interferogram will have a one-to-one mapping from the path difference domain to the time domain via the mirror velocity. Thus, the movable mirror in the interferometer can be driven at a constant velocity. The recombined modulated beam reaches a concave mirror that focuses it on the surface of the sample. The sample absorbs part of the intensity of the beam, the other part being transmitted. The intensity of the reflected light is very small and usually is ignored. As the transmitted beam reaches the IR detector, the signal is automatically send to the computer, where it is Fourier transformed in order to obtain the infrared absorption spectrum. All data acquisition and manipulation are performed with “OPUS/IR” and “OPUS/Raman” software.

3.9 An alpha 300 WITec confocal Raman Spectrometer

For kidney stone samples, Raman measurements were recorded with an alpha 300 WITec confocal Raman system (see Figure 3.19), using the 532 nm excitation of a Nd:YAG laser. The acquisition time for each spectrum was 5 seconds and a 100 X objective lens with a N.A. = 0.95 was used in all experiments. The optical diagram of the system is shown in Figure 3.20.
Figure 3.19: An alpha 300 WITec confocal Raman system.

Figure 3.20: Schematic of an alpha 300 WITec confocal Raman system.
3.10 X-ray Photon Spectroscopy (XPS)

X-Ray Photon Spectroscopy (XPS) also known as “ESCA”; an abbreviation for Electron Spectroscopy for Chemical Analysis was invented by Nobel Prize winner Swedish physicist K. Siegbahn and his research group. In 1954, they recorded the first high energy resolution XPS spectrum of cleaved sodium chloride (NaCl) demonstrating the potential of XPS. The phenomenon is founded on the photoelectric effect as explained by Einstein, in which the concept of the photon was used for the explanation of expulsion of electrons from a surface when photons impose upon it. An ultra-high vacuum condition is required for XPS [164].

X-Ray photoelectron spectroscopy, a quantitative spectroscopic technique, is used for the measurement of elemental composition, empirical formula, chemical state and electronic state of the elements which are present on a material’s surface. XPS spectra are attained through irradiation of a material by a beam of aluminum or magnesium X-rays while simultaneously measuring the kinetic energy (K.E.) and number of electrons that escape from the top1 to 10 nm of the material being analyzed. For XPS, though, other x-ray lines such as Titanium K-alpha (2040 eV) can be used; Aluminum K-alpha (1486.6 eV) or Magnesium K-alpha (2040 eV) are generally preferred for the photon energies.

XPS is thus a surface chemical analysis technique. It is used for the analysis of the surface chemistry of a material, either in its “as received” state, or after certain treatments such as fracturing, cutting, or scraping, or after exposure to heat to study the changes due to heating, exposure to reactive gases and so on.

With the help of XPS, it is possible to detect all elements with an atomic number (Z) of 3 and above. However; it can not detect elements with atomic number z=1 (hydrogen) and z=2 (helium). For a majority of the elements, XPS has a detection limit in the parts per thousand
range. However, it is possible to achieve the detection limit of parts per million (ppm), but it requires conditions such as a high X-ray flux at the sample surface or a very long collection time i.e. overnight. Generally, XPS finds applications for the analysis of samples including but not limited to inorganic compounds, polymers, elements, metal alloys, semiconductors, ceramics, paints, papers, inks, woods plant parts, catalysts, glasses, make-up items, teeth, bones, viscous oils, glues, ion modified materials, and so on.

The types of information that XPS analysis can provide include finding the elemental composition of the surface, empirical formulas of pure materials, elements that contaminate a surface, the chemical or electronic state of each element in the surface, the uniformity of elemental composition on a top surface and the uniformity of elemental composition as a function of ion beam etching [164].

3.10.1 Physics of X-Ray Photoelectron Spectroscopy

Photoelectron spectroscopy is based upon a single photon in and electron out process and hence, from many perspectives, this fundamental process is a much simpler phenomenon than the one on which Auger spectroscopy is based [165].

Monochromatc sources of radiation (i.e. photons of fixed energy) are used in photoelectron spectroscopy. The energy of a photon is given by the Einstein relation;

$$E_{\text{Photon}} = h \nu$$

(3.5)

where; $h$ is Planck’s constant and $\nu$ is the frequency of the radiation in Hz.

In XPS an atom in a molecule or solid absorbs the photon, leading to ionization and the emission of an electron from the inner shell. The kinetic energy distribution of emitted photoelectrons can be measured using any appropriate electron analyzer and thus, a photoelectron spectrum can be recorded [166].
The process of photo-ionization can be considered as follows;

\[ A + E_{\text{photon}} = A^+ + e^- \]  \hspace{1cm} (3.6)

Now, according to the law of conservation of energy;

\[ E(A) + E_{\text{photon}} = E(A^+) + E(e^-) \]  \hspace{1cm} (3.7)

Since the electron’s energy is present entirely as kinetic energy, this can be rearranged in terms of the kinetic energy of the photoelectron;

\[ E(e^-) = E_{\text{Kinetic}} = E_{\text{photon}} - [E(A^+) - E(A)] \]  \hspace{1cm} (3.8)

The term in brackets is nothing but the difference in energy between the ionized and neutral atoms; it is generally called the binding energy of the electron, which leads to the following expression,

\[ E_{\text{Kinetic}} = E_{\text{photon}} - E_{\text{Binding}} \]  \hspace{1cm} (3.9)

The binding energy is now taken to be a direct measure of the energy required to just remove the electron from its initial level to the Fermi level of the solid sample and the kinetic energy of the photoelectron is again expressed as,

\[ E_{\text{Kinetic}} = E_{\text{photon}} - E_{\text{Binding}} - \Phi \]  \hspace{1cm} (3.10)

where \( \Phi \) is called the work function of the sample and is the energy needed to raise the electron from the Fermi level to the vacuum level.

A characteristic XPS spectrum, which is shown in Figure 3.22, is a plot of the number of electrons detected versus the binding energy of the electrons detected. Each element creates a typical set of XPS peaks at characteristic binding energy values that directly identify each element that is present in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron arrangement of the electrons within the atoms such as 1s, 2s, 2p,
3s and so on. The number of detected electrons in each of the characteristic peaks is directly related to the amount of the corresponding element within the volume irradiated. In order to produce atomic percent values, each raw XPS signal needs to be corrected, which can be achieved by dividing its signal intensity by a “relative intensity factor” (RSF) and normalizing over all of the elements detected.

Figure 3.21: Energy diagram for XPS phenomenon
Since electron counting detectors in XPS characterizations are usually about one meter away from the material irradiated by X-rays, it is quite essential to perform the XPS measurement under high vacuum in order to count the number of electrons at each kinetic energy value.

![Characteristic XPS spectrum](image)

**Figure 3.22:** Characteristic XPS spectrum

It is imperative to note that XPS detects only those electrons that have actually escaped into the vacuum of the instrument and mostly these electrons have originated from within the top 10 to 12 nm of the material. All of the deeper photo-emitted electrons, which were generated as the X-ray penetrated 1-5 micrometers of the material, are either recaptured or trapped in various excited states within the material. Thus, none of the deeper photo-emitted electrons, which were created as the X-ray penetrated 1-5 micrometers of the material, are detected. For the majority of applications, this technique, indeed, is a nondestructive technique that measures the surface chemistry of any material.
3.10.2 XPS Instrumentation

The XPS system, as shown in **Figure 3.23**, includes a source of X-rays, an ultra-high vacuum (UHV) stainless steel chamber with UHV pumps, an electron collection lens, an electron energy analyzer, an electron detector system, a moderate vacuum sample introduction chamber, sample mounts, a sample stage and a set of stage manipulators.

**Figure 3.23:** Schematic representation of XPS instrumentation

3.10.3 Applications of XPS

XPS is one of the most important and extremely useful materials characterization techniques. It is used in a variety of fields and various different industries, including but not limited to Glass, Laser, Polymer and Plastic, Electronics, Biotech, Ceramic, Mineralogy, Mining, Computer, Thin-film coating, Semiconductor, Lighting, Welding, Battery, Beverage, Catalyst, Automotive, Agriculture, Adhesion, Nuclear, and so on.
Some of the important applications include:

- XPS characterization is used to determine the types of elements and quantity of the elements present within ~10 nm of the sample surface.
- XPS is used for the determination of the type of contamination, if any exists in the surface or the bulk of sample.
- XPS is also useful to determine the binding energies of one or more electron states
- The thickness of one or more thin layers of different materials within the top 10 nm of the surface can be determined with the help of XPS.
- It finds application to calculate the empirical formula of a material that is free of excessive surface contamination.
- By using XPS, the density of electronic states can be determined.

3.10.4 Limitations of XPS Characterization

3.10.4.1 Quantitative Precision Limit

- Signal to noise ration (S/N), peak intensity, accuracy of relative sensitivity factors, correction for electron transmission function, surface volume homogeneity, correction for energy dependency of electron mean free path, and degree of sample degradation due to analysis are important parameters which affect the Quantitative precision of this technique.
- Under the best possible circumstances, the quantitative correctness of the percentage values of the atoms calculated from the major XPS peaks is 90-95% of the atom% values of each major peak. If a high level quality control protocol is
used, the accuracy can be further improved. On the other hand, in a routine work environment, the accuracy ranges from 80-90% of the value reported in atom% values because in such a case the surface contains a mixture of contamination and expected material.

- And the quantitative precision for the weaker XPS signals, such as those having peak intensities 10-20% of the strongest signal, are 60-80% of the true value.

### 3.10.4.2 Detection Limits

- Generally, X-ray photoelectron spectroscopy exhibits a detection limit of 0.1-1.0 atom% at the surface, that is, it has limit of about 1 part per thousand (1,000 ppm). However, under the best conditions, for most elements, a detection limit of about 100 ppm can be achieved.

### 3.10.4.3 Analysis area limits

- The area of analysis is quite dependent on device blueprint. The smallest analysis area ranges from 10 to 200 micrometers in diameter. For a monochromatic beam of X-rays, a large size is 1-5 mm, whereas non-monochromatic beams are 10-50 mm in diameter. However, on the latest imaging XPS instruments using synchrotron radiation as the X-ray source, spectroscopic image resolution levels of 200 nm or below have been achieved.

### 3.10.4.4 Sample size limits

- In older devices the sample size limit was approximately a cm. However, with ultra modern instruments it is possible to analyze entire 300 mm wafers.

### 3.10.4.5 Degradation during analysis

- Sensitivity of the sample material to the wavelength of X-rays used and the total
dose of X-rays as well as the temperature of the surface and the level of the vacuum are parameters which can cause degradation during analysis. Either non-monochromatic or monochromatic X-rays cause measurable degradation of metals, alloys, ceramics and most glasses. However, both of them can cause degradation for some polymers, catalysts, certain highly oxygenated compounds, various inorganic compounds and fine organic samples.

- Non-monochromatic X-ray sources produce a significant amount of high energy Bremsstrahlung X-rays (1-15KeV of energy) which directly degrade the surface chemistry of various materials. Moreover, since the anode that produces the X-rays is characteristically only 1 to 5 cm away from the sample, non-monochromatic X-ray sources also convey a significant amount of heat (raising temperatures from 100 to 200 °C) to the surface of the sample. For certain materials, this high level of heat in combination with the high energy X-rays not only increases the amount of degradation but also the rate of degradation. On the other hand, since the monochromatic X-ray sources are farther away from the sample, they do not cause any heat effects. Moreover, in the case of a monochromatic source, the sample only encounters one X-ray energy.

- The chemistry and surface morphology will continue to change until the surface attains a stable state because, initially trapped within or on the surface of the sample, different gases such as O₂, CO, and liquids such as water or alcohol are removed by the vacuum. This type of degradation is sometimes hard to detect.
3.10.5 Materials routinely analyzed by XPS

XPS is utilized for the analysis of different types of materials such as metal alloys, semiconductors, polymers, pure elements, catalysts, glasses, ceramics, paints, papers, inks, woods, plant parts, make-up, teeth, bones, human implants, bio-materials, viscous oils, glues, and ion modified materials. Organic compounds are readily degraded by either the energy of the X-rays or the heat from a non-monochromatic X-ray source, so, generally XPS is not used for the analysis of organic chemicals.

3.11 Photoluminescence Spectroscopy

Photoluminescence spectroscopy is one of the most important materials characterization techniques and it has been extensively used for the measurement of various important material properties. It is a non-contact, nondestructive method of probing the electronic structure of materials. In this technique light is aimed onto a sample, where it is absorbed and passes its energy to the material. This process is termed photon-excitation. The sample may dissipate this excess energy through the emission of light, or luminescence. The spontaneous emission of light from a material under optical excitation is called photoluminescence (PL). The intensity and spectral content of this photoluminescence is a direct measure of various important material properties [166-168].

Because of photo-excitation, electrons move into permissible excited states within the material. These excited electrons may achieve equilibrium states through two different processes; either by a radiative process or by a nonradiative process. This means that the release of surfeit energy may include the emission of light or it may not. The energy of the emitted light depends on the discrepancy in energy levels between the two electron states involved in the conversion,
that is, between the excited state and the more stable state. The quantity of emitted light is related to the relative contribution of the radiative process.

When light with sufficient energy impinges on a sample, photons are absorbed and electronic excitations are produced. Ultimately, equilibrium is achieved as the electrons return to the ground state. If equilibrium is achieved through radiative relaxation, the emitted light is called photoluminescence. This light can be collected and investigated in order to obtain information about the photo-excited material. The transition energies can be obtained from PL spectra, and by using these values electronic energy levels can be found. The PL intensity is a measurement of the relative rates of radiative and nonradiative recombination. Variation of the PL intensity with external parameters, for instance, temperature and applied voltage, can be utilized for further characterization of the fundamental electronic states and bands.

Photoluminescence relies on optical excitation characteristics. Not only is the initial photo-excited state determined by the excitation energy, but also the penetration depth of the impinging light is governed by it. Photoluminescence signals depend consistently on the density of photo-excited electrons, which can be controlled through the intensity of the incident beam. When the type or quality of material under examination varies spatially, the photoluminescence signal will alter with excitation site. Moreover, pulsed optical excitation gives a powerful way to study transitory phenomena. Once the short laser pulses produce virtually instantaneous excited populations, the photoluminescence signal can monitored for determination of recombination rates.

3.11.1 Instrumentation for Photoluminescence

Photoluminescence is simple, versatile, and nondestructive. For normal photoluminescence, modest instrumentation is required, which usually contains an optical source
and an optical power meter or spectrometer. A typical photoluminescence set-up is demonstrated in Figure 3.24. Since, in this characterization, the measurement does not rely on electrical excitation or detection, it requires nominal sample preparation. This facet makes photoluminescence superb for materials with poor conductivity or undeveloped contact/junction technology.

![Figure 3.24: Typical experimental set-up for PL measurements](image)

The measurement of the continuous wave Photoluminescence intensity and spectrum is speedy and straightforward. However, transient Photoluminescence is more demanding, especially if recombination processes are rapid. Although, instrumentation for time-resolved detection, such as photon counting, can be expensive and complex, Photoluminescence is one of the only techniques available to study rapid transient behavior in materials.
3.11.2 Applications of Photoluminescence

3.11.2.1 Band Gap Determination

In semiconductors, commonly occurring radiative transition is between states in the conduction and valence bands, with the energy difference being known as the band gap. While working with new semiconductor compounds, band gap determination is found to be useful.

3.11.2.2 Impurity Levels and Defect Detection

In semiconductors, radiative transitions also include localized defect levels. With the help of photoluminescence energy associated with these levels, specific defects can be identified. Additionally, the quantity of photoluminescence can be used for the determination of their concentration.

3.11.2.3 Recombination Mechanisms

Recombination can include both radiative as well as nonradiative processes. The quantity of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. Hence, the fundamental physics of recombination mechanisms can be understood through the analysis of photoluminescence.

3.11.2.4 Quality of Materials

Generally, nonradiative processes are coupled with localized defect levels and the presence of it is unfavorable to material quality and subsequent device performance. Hence, material quality can be measured by quantifying the quantity of radiative recombination.

3.11.3 Special Features of Photoluminescence Spectroscopy

- A variety of excitation wavelengths allows different penetration depths into the material, and thus, varying levels of volume excitation
• Detection of photoluminescence from 0.4 to 2.8 micrometers using diffraction and Fourier-transform based systems.
• Sensitivity down to the level of parts per thousand, depending on impurity species and host.
• Sample temperatures of 4 to 300 K.
• Mapping capabilities with 1-micrometer spatial resolution on Fourier-transform based systems.

3.11.4 Pros of Photoluminescence

Photoluminescence can be used to study virtually any surface in any environment and hence, it can be used to watch changes induced by surface modification in real time. For instance, generally, photoluminescence, like most surface characterization techniques, is not sensitive to the pressure in the sample chamber. So, it can be used to study surface properties in relatively high-pressure semiconductor growth reactors. Since photoluminescence does not depend strongly on temperature, room temperature measurements are adequate for many purposes. However, liquid helium temperatures are required for the highest spectral resolution. Moreover, photoluminescence has minimal effect on the surface under examination. Although, photoinduced changes and sample heating are possible, this effect can be minimized, by using low excitation. In situ photoluminescence measurements do need optical access to the sample chamber. Nevertheless, compared to other optical techniques of characterization such as reflection and absorption, photoluminescence is flexible about beam alignment, surface flatness, and sample thickness.
3.11.5 Cons of Photoluminescence

The main shortcoming of photoluminescence characterization also follows from the dependence on optical technique; i.e. the sample under investigation must emit light. Indirect-bandgap semiconductors have innately low photoluminescence efficiency. In such materials, nonradiative recombination tends to dominate the relaxation of excited populations. This problem can be amplified by poor surface quality, where swift nonradiative events may arise. However, once a PL signal is detected, it can be used for the characterization of both radiative and nonradiative phenomena. Although it may be impossible to identify directly the nonradiative traps by PL, their signature is obvious in various categories of PL measurements.

The problem in estimating the densities of interface and impurity states is another disadvantage of photoluminescence. When these states have radiative levels, they are readily identified in the photoluminescence spectrum, and the size of the associated PL peaks gives a relative measure of their presence in the sample. However, measuring the absolute density of these states is a far more difficult task and typically requires a meticulous analysis of the excitation intensity dependence of the PL signal [168]

3.11.6 Confocal Photoluminescence Spectroscopy

When a laser is aimed at a sample, the smallest spot size is decided by the diffraction limit, which is roughly equivalent to the wavelength of the laser light. For the analysis of semiconductors, the optical excitation energy must be higher than the bandgap. Since, generally, this corresponds to wavelengths in the visible or near infrared, the diffraction limited spot size is of the order of 1 μm. When carrier diffusion is not present, the spatial resolution of Photoluminescence measurements is governed by the excitation spot size. Yet, photogenerated
carriers frequently diffuse average distances much larger than 1 mm before recombining. Hence, photoluminescence is generated in a broader region than the original excitation spot. Restricting the PL collection time can circumvent diffusion-limited spatial resolution.

The easiest way to overcome this difficulty is a Photoluminescence extension of confocal microscopy. In this technique, enhanced spatial resolution, improved depth profiling, and insensitivity to scattered light are achieved by using matched illumination and collection optics with back focal plane apertures.

**3.11.7 Importance of Photoluminescence**

In this technique, in order to explore different regions and excitation concentrations in the sample, the excitation energy and intensity are chosen. Photoluminescence study can be used for the characterization of various material parameters. PL spectroscopy offers electronic characterization rather than mechanical characterization. PL is a selective and exceptionally sensitive probe of distinct electronic states. Characteristics of the photoluminescence spectrum can be used for the identification of surface, interface, and impurity levels. By using this spectroscopy, it is also possible to gauge alloy disorder and interface roughness. Moreover, the information on the quality of surfaces and interfaces can be obtained through the intensity of the PL signal. Under pulsed excitation, the momentary PL intensity yields the lifetime of nonequilibrium interface and bulk states. Under an applied bias, variation of the PL intensity can be used for the mapping of the electric field at the surface of a sample. Additionally, thermally activated processes cause alterations in PL intensity with temperature [168].

In conclusion, PL investigation is nondestructive. In fact, PL requires minimal sample treatment or environmental control. Since sample excitation is achieved optically, electrical
contacts and junctions are avoidable and high-resistivity materials cause no detectable inaccuracy. Moreover, since time-resolved PL can be very fast, it is useful for the characterization of the most rapid processes in a material. However, PL analysis exhibits certain fundamental limitation due to its dependence on radiative events. Material with reduced radiative efficacy, such as low-quality indirect band-gap semiconductors are challenging to study by using normal PL. In a similar manner, detection of impurity and defect states relies on their optical activity. Although PL is a very insightful probe of radiative levels, one must rely on secondary evidence to study states that couple faintly with light.

3.13 Horiba-Jobin Yvon INDURAM Spectrometer

The photoluminescence measurements were performed with a Horiba Jobin-Yvon Raman micro-probe system. An incident 632.8 nm He-Ne laser excitation was used at a power of less than 10 mW. The acquisition time for each spectrum was 64 s.

Figure 3.25: Horiba Jobin Yvon INDURAM spectrometer.
Figure 3.26: Optical diagram for Horiba Jobin Yvon INDURAM system
CHAPTER 4

SPECTROSCOPIC CHARACTERIZATION OF L-ARGININE DOPED POTASSIUM DIHYDROGEN PHOSPHATE CRYSTALS

4.1 FT-IR Spectroscopic Investigation

The infrared spectrum of any given substance is interpreted by the use of characteristic absorption bands associated with different functional groups. Furthermore, the vibrational absorption lines may be associated with stretching vibrations, which involve bond length changes, or deformation vibrations, which involve bond-angle changes of such structures. Typically, for a given functional group, the vibrational bands due to stretching occur at higher frequencies than those due to deformation. This is due to the need for more energy for stretching groups than for deforming them, where the bonding forces oppose the shape changes [169].

Although functional group vibrational frequencies occur within “narrow” limits, interference or perturbations may cause a shift of characteristic bands as a result of the electronegativity of neighboring groups or atoms, the spatial geometry of the molecule, or the mechanical mixing of vibrational modes. Also, sometimes, functional groups have more than one characteristic absorption band associated with them. On the other hand, two or more functional groups can absorb in the same region. In general, they can only be distinguished from each other by means of other characteristic infrared bands, which present non-overlapping regions.

Commonly, since most of the samples contain carbon, the absorption bands may be considered as having two main fundamental vibration regions, such as the one of the C=O, C=C,
CH₂, and CH₃ groups, and the one of the C-C-C-C skeletal groups (the molecular backbone or skeleton of the molecule).

The infrared absorption spectra recorded in the current work for the pure KDP and the 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped crystals are presented in Figure 4.1. The samples were prepared in the form of pellets by embedding the materials in a KBr polycrystalline matrix. It is apparently clear that the results are quite similar for the crystals without and with L-arginine incorporation, except for the appearance of new weak peaks in the latter. Also, as the concentration of L-arginine doping increases, these peak intensities become slightly more intense. Due to the better visibility of these vibrational lines, below we will concentrate on discussing the outcome of our results in terms of the sample prepared with the highest L-arginine concentration, e.g. 0.5 wt% L-arginine doped KDP crystals.

The infrared transmission data in the 400 – 2000 cm⁻¹ range for the standard KDP and for the 0.5 wt% L-arginine doped KDP crystals are presented in Figure 4.2(a). For comparison purposes we also performed the infrared measurements for an L-arginine amino acid reference sample, which is presented in Figure 4.2(b). A glance at the spectra of standard and doped KDP crystals reveals that the main absorption bands at 537 cm⁻¹, 900 cm⁻¹, 1098 cm⁻¹, 1297 cm⁻¹, and 1677 cm⁻¹ are characteristic of the KDP crystal. Besides the main characteristics peaks of KDP, several extra peaks such as 1401 cm⁻¹, 1637 cm⁻¹, and 1716 cm⁻¹ can be observed in the spectra of the L-arginine doped KDP crystal. The occurrence of these additional vibrational lines is direct evidence of successful L-arginine doping. The main vibration bands corresponding to the KDP crystals at 537 cm⁻¹ is attributed to the POH deformatinal vibration and the vibration band at 900 cm⁻¹ is attributed to the asymmetrical PO₂(H₂) vibration. Further assignment of vibration bands reveals that the vibration band at 1098 cm⁻¹ is attributed to the asymmetrical PO₄
vibration, the vibration band at 1297 cm\(^{-1}\) corresponds to the deformational PO\(_4\) vibration and the vibration band at 1677 cm\(^{-1}\) is attributed to the combinational type. The assignments of the vibrational lines of pure KDP are summarized in Table 4.1.

Figure 4.1: FT-IR spectra for pure and 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped KDP crystals as labeled.
Figure 4.2: Infrared transmission data between 400 and 2000 cm\(^{-1}\) for (a) standard KDP and 0.5 wt% L-arginine doped KDP crystals, and (b) L-arginine reference sample.

The examination of the absorption spectrum of the L-arginine reference sample in Figure 4.2(b) reveals that a medium band at 1138 cm\(^{-1}\) can be attributed to wagging NH\(_2\). The band at
1188 cm$^{-1}$ can be attributed to the NH$_3^+$ rocking mode. Actually, the existence of this vibrational band proves the protonation of the amino group attached to the $\alpha$-carbon atoms [170]. The occurrence of vibrational bands at 771 cm$^{-1}$ can be attributed to wagging NH, which provides the evidence for the presence of the N-H group [171]. The vibrational band at 493 cm$^{-1}$ is due to rocking COO$^-$ and at 547 cm$^{-1}$ is due to wagging COO$^-$, providing the evidence for the ionization of the carboxyl group. The occurrence of vibrational bands at 1682 cm$^{-1}$ provides the evidence for the presence of the C=N absorption band. The vibrational band at 1638 cm$^{-1}$ is attributed to the NH$_3^+$ asymmetric deformation and the vibrational band at 1138 cm$^{-1}$ is attributed to the wagging NH$_2$. The assignments of the vibrational bands for L-arginine are summarized in Table 4.2

In the infrared absorption spectra of L-arginine doped KDP crystals, several extra vibrational lines such as at 1401 cm$^{-1}$, 1637 cm$^{-1}$ and 1716 cm$^{-1}$ can be observed as compared to the infrared absorption spectra of the pure KDP crystal. The comparison of the new features with the characteristic bands of L-arginine demonstrates that the 1401 cm$^{-1}$ line can be attributed to a combination of the downshifted lines at 1421 cm$^{-1}$, at 1474 cm$^{-1}$, and at 1558 cm$^{-1}$. Among these vibrational peaks of the L-arginine reference sample, the vibrational peak at 1421 cm$^{-1}$ is attributed to the CH$_2$ asymmetric vibration, the vibrational peak at 1474 cm$^{-1}$ is attributed to the C-H and N-H rocking vibrations and the vibrational peak at 1558 cm$^{-1}$ corresponds to the C-H and C-N stretching vibrations (please, see Table 4.3). The 1637 cm$^{-1}$ weak feature is coming from a combination of both the 1638 cm$^{-1}$ and the 1682 cm$^{-1}$ lines, both of which exhibit downshifting behavior [170, 171]. Among these vibrational bands, the vibrational band at 1638 cm$^{-1}$ corresponds to the NH$_2$ asymmetrical deformation and the vibrational band at 1682 cm$^{-1}$ to
the C=N absorption band. The definite presence of the C=O asymmetric stretching vibration at 1716 cm\(^{-1}\) is marked in Figure 4.2 by a double arrow.

Table 4.1  The assignment of the infrared vibrational lines of pure KDP (In 400 - 1600 cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
<th>Experimental (cm(^{-1}))</th>
<th>Ref. 212 (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>537</td>
<td>536.2</td>
<td>POH deformational vibration</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>909.4</td>
<td>asymmetrical PO(_2)(H(_2)) vibration</td>
<td></td>
</tr>
<tr>
<td>1098</td>
<td>1098.8</td>
<td>asymmetrical PO(_4) vibration</td>
<td></td>
</tr>
<tr>
<td>1297</td>
<td>1302.1</td>
<td>deformational PO(_4) vibration</td>
<td></td>
</tr>
<tr>
<td>1677</td>
<td>1696.1</td>
<td>combinational type</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2  The assignment of the infrared vibrational lines of L-arginine (In 400 - 1600 cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
<th>Experimental (cm(^{-1}))</th>
<th>Ref.170 (cm(^{-1}))</th>
<th>Ref.171 (cm(^{-1}))</th>
<th>Ref.172 (cm(^{-1}))</th>
<th>Ref.181 (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>493</td>
<td>493.29</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>rocking COO</td>
</tr>
<tr>
<td>547</td>
<td>550.81</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>wagging COO</td>
</tr>
<tr>
<td>771</td>
<td>753.8</td>
<td>777</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>wagging NH</td>
</tr>
<tr>
<td>1138</td>
<td>1136.47</td>
<td>1133</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>wagging NH(_2)</td>
</tr>
<tr>
<td>1188</td>
<td>1188.03</td>
<td>1178</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>NH(_3^+) rocking mode</td>
</tr>
<tr>
<td>1421</td>
<td>---</td>
<td>1418</td>
<td>1423.77</td>
<td>---</td>
<td>---</td>
<td>CH(_2) asymmetric vibrations</td>
</tr>
<tr>
<td>1474</td>
<td>---</td>
<td>---</td>
<td>1473.65</td>
<td>---</td>
<td>---</td>
<td>C-H and N-H rocking vibrations</td>
</tr>
<tr>
<td>1558</td>
<td>1562.44</td>
<td>---</td>
<td>1556.08</td>
<td>---</td>
<td>---</td>
<td>C-H and C-N stretching vibrations</td>
</tr>
<tr>
<td>1638</td>
<td>1645.29</td>
<td>---</td>
<td>1635.2</td>
<td>1633.2</td>
<td>---</td>
<td>NH(_2) asymmetrical deformation</td>
</tr>
<tr>
<td>1682</td>
<td>1684.66</td>
<td>---</td>
<td>1683</td>
<td>---</td>
<td>---</td>
<td>C=N absorption band.</td>
</tr>
<tr>
<td>1716</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1722</td>
<td>---</td>
<td>C=O asymmetric stretching vibration</td>
</tr>
</tbody>
</table>
Table 4.3  The assignment of the infrared vibrational lines of L-arginine doped KDP (In 400 - 1600 cm$^{-1}$).

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental (cm$^{-1}$)</strong></td>
</tr>
<tr>
<td><strong>AR+KDP</strong></td>
</tr>
<tr>
<td>1401</td>
</tr>
<tr>
<td>1474</td>
</tr>
<tr>
<td>1558</td>
</tr>
<tr>
<td>1637</td>
</tr>
<tr>
<td>1682</td>
</tr>
<tr>
<td>1716</td>
</tr>
</tbody>
</table>

The infrared transmission spectra in the 2200-3600 cm$^{-1}$ region for standard and 0.5 wt% L-arginine doped KDP crystals are shown in Figure 4.3 (a). As was done above in a different frequency region, in Figure 4.3(b), the spectrum of the standard L-arginine sample is also presented.

In this wavenumber region, the infrared absorption spectrum of pure KDP exhibits the vibration bands at 2462 cm$^{-1}$ and at 3432 cm$^{-1}$, which are attributed to the O-H bands. (see Table 4.4). In the case of L-arginine, the charged L-arginine is characterized by the protonated [(H$_2$N)$_2$CNH]$^+$ guanidyl group, the protonated alpha-amino group NH$_3^+$ and the deprotonated carboxylate group COO$^-$. For arginine salts, certain peaks in the wavenumber region between 2800 and 3400 cm$^{-1}$ are characteristic of the CH$_2$ stretching vibrations and NH$_3^+$ alpha-amino lines [170-172]. The infrared absorption spectrum of the L-arginine reference sample reveals vibrational lines at 2864 cm$^{-1}$, 2948 cm$^{-1}$, 3070 cm$^{-1}$, 3302 cm$^{-1}$ and 3370 cm$^{-1}$. Among these, the vibrational bands at 2864 cm$^{-1}$, 2948 cm$^{-1}$ and 3070 cm$^{-1}$ can be attributed to CH$_2$ lines of L-
arginine. The vibrational line at 3302 cm\(^{-1}\) and at 3363 cm\(^{-1}\) can be attributed to the N-H vibrations from NH\(_2\) and NH\(_3^+\) bands. The assignments of the absorption bands for the L-arginine salts are summarized in Table 4.5

![Figure 4.3](image)

**Figure 4.3**: Infrared transmission data in the 2200 - 3600 cm\(^{-1}\) range for: (a) standard KDP and 0.5 wt% L-arginine doped KDP crystals, and (b) L-arginine reference sample.
The vibrational peaks at 2462 cm\(^{-1}\) and 3432 cm\(^{-1}\), which can be observed in the KDP spectrum, are attributed to the O-H bands. In addition to these vibrational lines, other very weak vibrations at 2854, 2925, and 3008 cm\(^{-1}\) also can be observed in the spectrum of L-arginine doped material and comparison of these new features with the characteristic bands of L-arginine demonstrates that these vibrational lines are associated with the CH\(_2\) lines of L-arginine at 2864, 2948, and 3070 cm\(^{-1}\) and shifted toward the lower energies by 10, 23 and 62 cm\(^{-1}\), respectively (see, **Table 4.6** [170-172]). Moreover, apparently another vibrational line at 3127 cm\(^{-1}\) can be observed in the spectrum of KDP with 0.5 wt% L-arginine. The existence of this vibrational line carries significant importance because it is attributed to a combination of N-H vibration from NH\(_2\) and NH\(_3^+\) bands around the 3300 cm\(^{-1}\) region that are also downshifted to a lower energy [170-172].

**Table 4.4** The assignment of the infrared vibrational lines of pure KDP (In 2000 - 3600 cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
<th>Experimental (cm(^{-1}))</th>
<th>Ref.212 (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>O-H bands</td>
</tr>
<tr>
<td>2462</td>
<td>2462</td>
<td>2463</td>
<td>O-H bands</td>
</tr>
<tr>
<td>3432</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.5** The assignment of the infrared vibrational lines of L-arginine (In 2000 - 3600 cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
<th>Experimental (cm(^{-1}))</th>
<th>Ref.170 (cm(^{-1}))</th>
<th>Ref.171 (cm(^{-1}))</th>
<th>Ref.172 (cm(^{-1}))</th>
<th>Ref.181 (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH(_2) asymmetric stretching</td>
</tr>
<tr>
<td>2864</td>
<td>---</td>
<td>2860</td>
<td></td>
<td>2876.14</td>
<td>---</td>
<td>CH(_2) symmetric stretching</td>
</tr>
<tr>
<td>2948</td>
<td>---</td>
<td>2958</td>
<td>2944.47</td>
<td>2979.5</td>
<td>---</td>
<td>CH(_2) symmetric stretching</td>
</tr>
<tr>
<td>3070</td>
<td>---</td>
<td>3084</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>NH(_2^+) stretching</td>
</tr>
<tr>
<td>3302</td>
<td>3289.01</td>
<td>3298</td>
<td>3295.58</td>
<td>---</td>
<td>---</td>
<td>NH(_3^+) asymmetric stretching</td>
</tr>
<tr>
<td>3363</td>
<td>---</td>
<td>3380</td>
<td>3391</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>
The assignments of L-arginine bands were done by comparison with the available literature on typical vibrational lines of arginine salts [170-172], as well as by simulation. The experimental results and those computed by Gaussian software are presented in Figure 4.4 (a) and (b), for infrared absorption and Raman, respectively. A specific B3LYP/6-31G* method of the density functional theory calculations was employed for simulation, since this hybrid method was found to give the best agreement with the experimental data. From Figure 4.4 (a) and (b), it is apparent that our experimental results are in good agreement with the simulated results.

<table>
<thead>
<tr>
<th>Experimental (cm⁻¹)</th>
<th>Ref.170 (cm⁻¹)</th>
<th>Ref.171 (cm⁻¹)</th>
<th>Ref.172 (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR+KDP 2854</td>
<td>2860</td>
<td>2876.14</td>
<td>CH₂ asymmetric stretching</td>
<td></td>
</tr>
<tr>
<td>L-AR 2925</td>
<td>2958</td>
<td>2944.47</td>
<td>CH₂ symmetric stretching</td>
<td></td>
</tr>
<tr>
<td>3008</td>
<td>3084</td>
<td>---</td>
<td>CH₂ symmetric stretching</td>
<td></td>
</tr>
<tr>
<td>3127</td>
<td>3289.01</td>
<td>3295.58</td>
<td>NH₂⁺ stretching</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3380</td>
<td>3391</td>
<td>NH₃⁺ asymmetric stretching</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6 The assignment of the infrared vibrational lines of L-arginine doped KDP (In 2000 - 3600 cm⁻¹)
Figure 4.4: Comparison for L-arginine reference sample of (a) experimental infrared transmission spectrum and calculated infrared absorption spectrum, and (b) experimental and calculated Raman spectra.
4.2 Raman Spectroscopic Characterizations

Two different approaches were employed for these measurements. Initially, the crystals of pure and doped KDP were positioned under the excitation laser beam and properly focused. While the standard KDP spectrum was recorded with no difficulties, different spectra were obtained in different spots on a single doped KDP crystal. The results reveal a strong inhomogeneous doping (please see Figure 4.5).

![Figure 4.5: FT-Raman spectra of 0.5 wt% L-arginine doped KDP crystal recorded at different spots on the sample.](image)
To overcome this problem, in the second approach, the powder samples of the pure KDP crystal and those with different concentrations of L-arginine were placed into a small metal container, which was then mounted in the spectrometer in a specially constructed holder. However, the differences seen in the Raman spectra for samples with different L-arginine doping concentrations were not consistent. Therefore, from now on, we consider for analysis only the Raman spectra of the sample with 0.5 wt% L-arginine doping and that of the standard KDP crystal as well as of the L-arginine reference sample. The Raman spectroscopic characterizations for these samples are presented in Figure 4.6 for the low frequency region.

**Figure 4.6:** Lower frequency region comparison of Raman spectrum of L-arginine doped KDP sample with Raman spectra of reference samples.
The main peak at 916 cm\(^{-1}\) in the Raman spectrum of the pure KDP crystal is associated with the asymmetrical P(OH)\(_2\) stretching mode and it is the “fingerprint” of the KDP material. It is characteristic of the internal vibrational mode at 912 cm\(^{-1}\) of the H\(_2\)PO\(_4\) anion in an aqueous solution of KH\(_2\)PO\(_4\) [173, 174]. Also, there are other characteristic lines of inorganic KDP, such as the peaks at 363, 474, and 549 cm\(^{-1}\), which correspond to the in-plane P(OH)\(_2\) and PO\(_2\) bending vibrations [173-175]. The assignments of the Raman vibrational lines of KDP materials are summarized in Table 4.7.

The effect of the pH values on the Raman active lattice modes of KDP has been studied in detail by M. Badrouj et al. [175] during their study of the pH dependent KDP growth rate. For KDP crystals, three wavenumber regions of 30–300, 300–1100 and 1100–3500 cm\(^{-1}\) are related to external vibrations, internal vibrations and hydrogen-bond vibrations, respectively [175].

Among these vibrational modes, internal vibrational modes (in the 300-1100 cm\(^{-1}\) region) are related to the vibrations of atoms in the interior of the crystal lattice. Each H\(_2\)PO\(_4\)\(^{-1}\) anion exhibits four internal vibrational modes, (1) the \(v_1= 920\) cm\(^{-1}\) band, which is more prominent as compared with others, is attributed to PO\(_4^{3-}\) symmetrical stretching vibrational modes, (2) the \(v_2=365\) cm\(^{-1}\) band is related to P(OH)\(_2\) bending vibration modes, (3) the \(v_3=572\) cm\(^{-1}\) band corresponds to PO\(_2\) bending vibration modes, and (4) the \(v_4=477\) cm\(^{-1}\) band is attributed to asymmetrical stretching vibrational modes. The distortion of H\(_2\)PO\(_4\)\(^{-1}\) will result in line broadening and even splitting. Of course, \(v_1\) and \(v_2\) bands do not split but they may be broadened. According to this study, different internal and external vibrational modes and local and instantaneous symmetry of PO\(_4^{3-}\) tetrahedrons are functions of parameters such as pressure, temperature and the type of experimental scattering geometry [175].
A multitude of vibrational lines in the 300 – 1600 cm\(^{-1}\) region can be observed in the Raman spectrum of the L-arginine. These vibrational lines are associated with vibrations of amino and carboxylate groups. Their assignments reveal that the vibrational bands at 554 cm\(^{-1}\), 619 cm\(^{-1}\) originate from the C-skeleton bands of L-arginine and the vibrational line at 859 cm\(^{-1}\) corresponds to the C-skeleton rocking vibration. The occurrence of the vibrational line at 882 cm\(^{-1}\) is due to the C-N and N-H stretching. The C-C-C skeleton exhibits characteristic vibrations in the range 1182-885 cm\(^{-1}\) [171]. Similar assignments of characteristic bands demonstrate that the vibrational line at 987 cm\(^{-1}\) corresponds to the N-H stretching, the vibrational band at 1069 cm\(^{-1}\) to the C-C-N stretching, and the vibrational band at 1108 cm\(^{-1}\) to a combination of COO\(^-\) and NH\(_2\) vibrations. The line at 1194 cm\(^{-1}\) is attributed to the C-N rocking and the vibrational band at 1309 cm\(^{-1}\) is due to a combination of N-H rocking and C=O stretching vibrations. The assignments of vibrational lines for L-arginine salts are summarized in Table 4.8

Comparison of the Raman spectrum of the 0.5 wt% L-arginine doped KDP sample with the spectra of the two standard samples allows assignment of the observed peaks. The vibrational lines at 363, 474, 549, and 916 cm\(^{-1}\) are attributed to the phosphate bands of KPD. The vibrational peaks at 363, 474, and 916 cm\(^{-1}\) do not demonstrate any noteworthy changes in their positions. However, a shift by around 19 cm\(^{-1}\) towards lower frequency is observed for the maximum of the broad line at 549 cm\(^{-1}\). The presence of L-arginine C-skeleton bands at 554 and 619 cm\(^{-1}\) might have influenced this maximum position and hence, it might be responsible for this shifting behavior. Moreover, in the 800 – 1500 region several changes can be observed for L-arginine vibrations. As examples, shifts to lower energies are seen for the C-skeleton rocking vibration at 859 cm\(^{-1}\), the C-N and N-H stretching at 882 cm\(^{-1}\), and the C-N rocking at 1194 cm\(^{-1}\). Besides shifting, a near disappearance is observed for the peaks at 987 cm\(^{-1}\) (N-H stretching),
1069 cm\(^{-1}\) (combination of N-H and C-C bonds), and 1108 cm\(^{-1}\) (combination of COO\(^{-}\) and NH\(_2\) vibrations). Also, the L-arginine lines at 1309 cm\(^{-1}\) (combination of N-H rocking and C=O stretching vibrations) and 1443 cm\(^{-1}\) (C-H bonds) exhibit higher frequencies in the doped sample. The assignments of vibrational lines for L-arginine salts are summarized in Table 4.9.

**Table 4.7** The assignment of the Raman vibrational lines of pure KDP (In lower frequency region).

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Experimental</strong></td>
<td><strong>Ref.173</strong></td>
</tr>
<tr>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
</tr>
<tr>
<td>363</td>
<td>363</td>
</tr>
<tr>
<td>474</td>
<td>475</td>
</tr>
<tr>
<td>549</td>
<td>549</td>
</tr>
<tr>
<td>916</td>
<td>916</td>
</tr>
</tbody>
</table>

**Table 4.8** The assignment of the Raman vibrational lines of L-arginine (In lower frequency region).

<table>
<thead>
<tr>
<th></th>
<th><strong>Assignment</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>554</td>
<td>L-arginine C-skeleton bands</td>
</tr>
<tr>
<td>619</td>
<td>L-arginine C-skeleton bands</td>
</tr>
<tr>
<td>859</td>
<td>C-skeleton rocking vibration</td>
</tr>
<tr>
<td>882</td>
<td>the C-N and N-H stretching</td>
</tr>
<tr>
<td>987</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>1069</td>
<td>C-C-N stretching</td>
</tr>
<tr>
<td>1108</td>
<td>combination of COO(^{-}) and NH(_2) vibrations</td>
</tr>
<tr>
<td>1194</td>
<td>the C-N rocking</td>
</tr>
<tr>
<td>1309</td>
<td>combination of N-H rocking and C=O stretching vibrations</td>
</tr>
<tr>
<td>1443</td>
<td>CH(_2) asymmetric bending</td>
</tr>
</tbody>
</table>
Table 4.9 The assignment of the Raman vibrational lines of L-arginine doped KDP (In lower frequency region).

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental (cm&lt;sup&gt;-1&lt;/sup&gt;)</strong></td>
</tr>
<tr>
<td>AR+KDP</td>
</tr>
<tr>
<td>812</td>
</tr>
<tr>
<td>840</td>
</tr>
<tr>
<td>Disappear</td>
</tr>
<tr>
<td>Disappear</td>
</tr>
<tr>
<td>Disappear</td>
</tr>
<tr>
<td>1160</td>
</tr>
<tr>
<td>1329</td>
</tr>
<tr>
<td>1453</td>
</tr>
</tbody>
</table>

From Figure 4.7 it can be observed that the KDP material does not exhibit any vibrational bands in the higher frequency region. In short, KDP is featureless in this region. On the other hand, L-arginine has a multitude of characteristic bands. In this region, L-arginine exhibits bands caused by C-H stretching of CH and CH<sub>2</sub> groups (around 2900 cm<sup>-1</sup>) and N-H vibrations of NH, NH<sub>2</sub>, and NH<sub>3</sub><sup>+</sup> (around 3300 cm<sup>-1</sup>). The vanishing of L-arginine asymmetric NH and NH<sub>2</sub> vibrations of the amino and guanidyl groups at 3296 and 3371 cm<sup>-1</sup> observed in the Raman spectrum of the amino-acid doped crystal, together with the splitting evidence of the C-H bonding at 2860 cm<sup>-1</sup>, 2924 cm<sup>-1</sup>, and 2950 cm<sup>-1</sup> into peaks at 2838 cm<sup>-1</sup>, 2883 cm<sup>-1</sup>, 2908 cm<sup>-1</sup>, 2924 cm<sup>-1</sup>, and 2963 cm<sup>-1</sup>, lead us to the possibility of an interpretation in terms of hydrogen bonding between the organic amino-acid and the inorganic material. Two possibilities consistent with this assumption are schematically presented in Figure 4.8 (a) and (b), where energetic rearrangements of the L-arginine molecule due to possible hydrogen bonding configurations
between the nucleophilic $O^-$ of the phosphate units of KDP and the $NH_3^+$ groups of L-arginine are shown. Of course, other possibilities also exist for the sites of the hydrogen bonding referred to the structure of the L-arginine. Our previously analyzed infrared absorption data corroborate to provide additional evidence supporting this assumption.

![Figure 4.7: Higher frequency region comparison of Raman spectrum of L-arginine doped KDP sample with Raman spectra of reference samples.](image)

**Figure 4.7:** Higher frequency region comparison of Raman spectrum of L-arginine doped KDP sample with Raman spectra of reference samples.
### Table 4.10  The assignment of the Raman vibrational lines of L-arginine (In higher frequency region).

<table>
<thead>
<tr>
<th>Experimental (cm(^{-1}))</th>
<th>Ref.171 (cm(^{-1}))</th>
<th>Ref.172 (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3296</td>
<td>3290.98</td>
<td>3296</td>
<td>N-H vibrations of NH, NH(_2) and NH(_3^+)</td>
</tr>
<tr>
<td>3371</td>
<td>3385,17</td>
<td>3385</td>
<td>N-H vibrations of NH, NH(_2) and NH(_3^+)</td>
</tr>
<tr>
<td>2860</td>
<td>2869</td>
<td>2881</td>
<td>C-H bonds of CH and CH(_2)</td>
</tr>
<tr>
<td>2924</td>
<td>---</td>
<td>2931.15</td>
<td></td>
</tr>
<tr>
<td>2950</td>
<td>2948</td>
<td>2956.85</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4.11  The assignment of the Raman vibrational lines of L-arginine doped KDP (In higher frequency region).

<table>
<thead>
<tr>
<th>Vibrational Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental (cm(^{-1}))</strong></td>
</tr>
<tr>
<td>AR+KDP</td>
</tr>
<tr>
<td>Vanishing</td>
</tr>
<tr>
<td>Vanishing</td>
</tr>
<tr>
<td>2838</td>
</tr>
<tr>
<td>2883</td>
</tr>
<tr>
<td>2908</td>
</tr>
<tr>
<td>2924</td>
</tr>
<tr>
<td>2963</td>
</tr>
</tbody>
</table>
Figure 4.8: Schematic representations of possible interactions between L-arginine and KDP in the doped sample. (a) Hydrogen bonding between O$^-$ of KDP phosphate unit and NH$_3^+$ of L-arginine guanidyl group. (b) Similar hydrogen bonding between KDP phosphate O$^-$ and L-arginine amino NH$_3^+$.

The results of our analysis indicate that structural changes are taking place for the L-arginine molecule as a result of its interaction with the KPD crystal. Both infrared and Raman spectroscopic techniques show disturbance of the N-H, C-H and C-N bonds of the amino acid, suggesting successful incorporation of L-arginine into the KDP crystals. However, only a
qualitative study was performed for the crystals, due to limitations arising from the strong inhomogeneity of the doped samples, which were synthesized using slow solvent evaporation growth techniques.

Here we suggest a possible model of hydrogen bonding between the oxygen of the KDP phosphate units and the NH$_3^+$ groups of the amino acid. This model was chosen as one of the simplest possibilities for accounting for the observed differences between infrared absorption and Raman spectra of the L-arginine doped sample as compared with the standard samples. The inherent complexity and the likely inhomogeneity of the doped sample presently preclude proposing that this model is a unique and necessary explanation for the data obtained to date. Possible future work towards placing greater constraints on the plausible sample structures for explaining the spectra might include crystallizing KDP doped with amino acids of simpler structure such as alanine to see which, if any, of the same or similar features appear in the spectra of the doped sample. We would expect such a comparison to provide further useful insight into this complex question.

4.3. Thermo Gravimetric Analysis (T.G.A.)

Thermogravimetry, a very useful technique for assessing the thermal stability of various substances [176-179], is based on the pyrolysis process, which often occurs through a many-stepped mechanism. The sample weight drops slowly as pyrolysis begins, and then drops precipitously over a narrow range of temperature, and finally, turns back to a zero slope as the reactants are used up.

While in many cases the thermogravimetric trace follows a characteristic common path for a wide range of decomposition processes, sometimes due to the overlap in the temperature
ranges from each mechanism step, an irregular weight-temperature curve, which may be difficult to analyze, can be obtained.

In the present report, the effect of L-arginine doping on the thermal stability of KDP crystals is also studied by this technique. The measured thermograms for pure, 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped KDP crystals are presented in Figures 4.9, 4.10, 4.11, and 4.12, respectively. A temperature variation from room temperature to 900°C, at a heating rate of 10°C/min, was employed. Also, for easier comparison, the combined thermograms are presented in Figure 4.13.

![Figure 4.9: Thermogram of pure KDP crystals.](image-url)
Figure 4.10: Thermogram of 0.3 wt% L-arginine doped KDP crystals

Figure 4.11: Thermogram of 0.4 wt% L-arginine doped KDP crystals.
Figure 4.12: Theromgram of 0.5 wt% L-arginine doped KDP crystals.

The thermogram of the pure KDP crystal presented in Figure 4.13 shows that the crystal is thermally stable up to 210°C (in an air atmosphere), the point where the dehydration process takes place. Upon heating, between 210°C and 240°C, a 3% weight loss from the evaporation of the constitutional liquid (water) on the crystal surface is observed. The thermal decomposition starts in the interior of the sample at a temperature above 285°C. The total weight loss for pure KDP crystals is around 11.65%, a loss that corresponds roughly to elimination of one water molecule for every KPO$_3$ unit [180]. Thus, initially, the crystal loses water of hydration, becoming anhydrous and remaining in that form up to the end of the analysis. Also, the large end residue observed in Figure 4.13 for pure KDP crystals might be attributed to phosphate products. This supposition is based on the reported literature results for temperatures higher than recorded in this TGA analysis, e.g. about 930°C, where intense phosphate decomposition weight loss has been observed [181].
A similar starting dehydration temperature of 210°C is revealed for L-arginine doped crystals. However, different water weight losses are observed with different doping concentrations. For example, a 5 wt% loss is seen for 0.3 wt% L-arginine doped crystals and 7 wt% losses are depicted for the other two L-arginine concentration amounts. These slight increases in the weight losses might be associated with the additional exclusion of NH\textsubscript{3} from L-arginine molecules. Also, above 285°C, the thermograms of the doped samples show major weight losses from decomposition of the main carbon chains, which at last will result in the formation of carbon dioxide [182].
Altogether, the doped crystals exhibit more weight losses than the pure KDP. We see that 12.63 wt%, 14.48 wt%, and 16.19 wt% weight losses are revealed by TGA analysis for the 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped crystals, respectively. Furthermore, with increasing doping these weight losses occur at slightly lower temperatures (of about 18°C lower) and more rapidly. This observation suggests that the increasing level of L–arginine doping speeds the decomposition process and weakens the KDP crystal, as expected, since amino acids become unstable at lower temperature. Also, this observation indirectly demonstrates the successful doping of the KDP crystals by L-arginine.
CHAPTER 5

SPECTROSCOPIC STUDY OF URINARY CALCULI

INHIBITION BY HERBAL EXTRACTS

In the present work, an attempt has been made to perform detailed scientific study of kidney stone formation and growth inhibition based on a traditional medicine approach with herbal extracts. In this regard, we have performed multi-technique spectroscopic investigations of these processes. Gel grown Pure and Rotula Aquatica Lour (RAL) incorporated calculi crystals were analyzed through different characterization techniques in order to obtain more insights as well as to understand the interaction mechanism between them. Raman, infrared absorption, X-ray photoelectron spectroscopy (XPS), and photoluminescence were employed to analyze the effects of RAL on the growth of magnesium-based calculi.

5.1 Importance of Multi-Technique Approach to the investigation for Calculi

For the analysis of human urinary stones, various different techniques such as chemical methods [185-187], infrared spectroscopy [185, 188 -190] X-ray powder diffraction [185, 191-194], and so on have been employed [185]. Furthermore, recently, Scanning Electron Microscopy also has been used. Though all of these techniques exhibit their efficacy, each of them have their noteworthy inherent confines and inadequacies [185, 195-197].
Generally, Chemical analysis is found to be unacceptable because it exhibits certain advantages, such as it is destructive and confusion exists as to the exact nature of the reactions taking place in qualitative tests, and because only atoms or groups of atoms instead of compounds may be identified. On the other hand, infrared investigations exhibit their own drawbacks such as they are limited to little representative pieces of the stone and cannot easily differentiate between the diverse phosphates that take place in urinary calculi. In addition to this, the powdering of stone samples is detrimental because certain components alter composition during the process of grinding [185]. In contrast to this, X-ray powder diffraction procedures can readily distinguish the different urates, oxalates and phosphates with confidence; however, they also possess specific disadvantages such as, in calculi of mixed composition, for example, one component may disguise the presence of another if the latter’s concentration is less than ~10%-20% of the sample. Commonly, apatite is awkward to recognize with X-ray diffraction and no difference between routinely observed hydroxyls and carbonates can be depicted by using this technique. Moreover, it also exhibits similar disadvantages to those of infrared spectroscopy in terms of sample preparation since it also requires the undesired powdering of the sample. Scanning electron microscopy with X-ray micro analysis capability is an extremely useful system for the examination of urinary calculi. However, with this technique it is extremely difficult to carry out the micro-analysis of elements lighter than Na. In short, since this technique requires a ground and polished surface for accurate quantitative analysis, it introduces the risk of compositional change during sample preparation [185].

In conclusion, each and every technique is thus independently insufficient to present an intimate image of stone composition and structure. In an attempt to acquire a complete and clear
picture of urinary calculi composition we have employed a multiple technique approach for the analysis of urinary calculi.

5.2 Detailed Analysis of the Effect of RAL Inhibitor on Crystal Size, Color, and Morphology

Good quality harvested crystals of pure as well as 1% and 2% RAL incorporated struvite crystals are shown in Figure 5.1. A quick glance at the crystals demonstrates there are drastic differences in size, color, and shape of the RAL incorporated calculi crystals. Hence, before we start our exploration, it would be quite worthwhile to carry out the physical study of the grown crystals. Later on we can corroborate our investigation results with our observations to obtain valuable information.

From Figure 5.1 it is apparently that as the amount of RAL inhibitor increases, the crystal sizes become smaller and smaller. In this sense Figure 5.1 serves as immediate evidence of the
decrease in crystal growth length with increasing *RAL* herbal extract concentration. From Figure 5.1, in addition to the dramatic decrease in crystal length, the change in crystal color also can be noticed. At this point, it would be quite important to note that there is an obvious color change from a white-transparent pure crystal to black-opaque crystals with inhibitor. This change in color is the obvious indication of the occurrence of chemical interaction between the crystal and inhibitor’s organic molecules. However, when we sectioned or crushed the *RAL* incorporated crystals, we observed that the crystals’ interiors did not exhibit the change in color and they were again white-transparent. Accordingly, we assume that the plant inhibitor directly contributes to impeding the growing process by passivating the crystal surface and forming a surface compound. In conclusion, instead of considering the inhibitor’s assimilation into the kidney stone crystal’s structure, here we have made an educated assumption about the surface compound formation. The legitimacy of our assumption of surface compound formation will be confirmed by the subsequent spectroscopic analysis.

Now, finally, there is merit to examining the crystal shapes presented in Figure 5.1. With our growth procedure, we were expecting to grow *ammonium magnesium hexahydrate* (*MgNH₄PO₄·6H₂O*), or struvite crystals. Generally, struvite (*MgNH₄PO₄·6H₂O*) crystals exhibit a variety of morphological shapes such as coffin, wedge-shape prism, and needles [198-200]. However, the crystals presented in Figure 5.1 do not exhibit such forms. Since they exhibit quite different morphological shape than struvite crystals, we believe that the grown crystals are probably not struvite crystals. Actually, the crystal shapes observed in Figure 5.1 closely resemble newberyite crystals obtained in a comprehensive study of the formation and transformation of struvites and newberyites by Babic-Ivancic et al. [201]. So, we presume that the products of the current work are more likely *newberyites* (*MgHPO₄·3H₂O*). According to
Babic-Ivancic’s explanation [201], pH control during the growth process is a critical factor in crystal formation. The authors have demonstrated that for a pH in the range between 5.0 and 7.0 the solid phase of newberyites is likely to be obtained, due to an abrupt decrease of the pH at the beginning of the chemical reaction. Additionally, intermediate reaction products may form due to the dehydration process before they transform to the more stable ammonium magnesium phosphate hexahydrate (struvite) [202]. Furthermore, there is no visible change in the morphology of crystals grown with the addition of RAL inhibitor. Since the occurrence of inhibitor in a crystal’s interior can affect the crystal’s manifestation, we also propose that more probably the RAL inhibitor is present only at the crystal’s surface and not in its interior.

In conclusion, the inhibitor has significant impact on the physical appearance of newberyite crystals. The incorporation of inhibitor into calculi crystals not only decreases the size of the crystals but also it changes their color. However, it does not affect the crystal morphology, that is, crystal morphology remains unchanged.

5.3 Raman Spectroscopic Characterization

Despite the fact that single crystal X-ray diffraction analysis can provide direct structural information, Raman and infrared absorption spectroscopic techniques proved to be useful in providing similar information. Moreover, with the help of these characterization tools, possible chemical bonding between inhibitor and crystal could be identified. The resultant room temperature Raman measurements of the crystals without and with RAL inhibitor are presented in Figure 5.2.

From Figure 5.2, it can be observed that there is a conspicuous increase in the Raman scattering background for the crystals with RAL. Specifically in the case of the 2% RAL
integrated crystal, an enormous increase in the Raman scattering is observed. This scattering occurs due to the inhibitor’s extremely high fluorescent character and it imposes the need for linear photoluminescence background subtraction, which was performed for such spectra. Due to the occurrence of this scattering background, it was not feasible to achieve satisfactory Raman spectra and, hence, results. Besides this dramatic scattering background increase, which unfortunately hindered obtaining good quality Raman data, no notable difference is observed with increasing inhibitor concentration.

![Raman spectra of crystals](image)

**Figure 5.2:** Raman spectra of crystals without and with 1% and 2% inhibitor, as labeled.
Other features at 409 cm\(^{-1}\), 501 cm\(^{-1}\), and 887 cm\(^{-1}\), attributed to the HPO\(_4\) bending motion, at 1056 cm\(^{-1}\), 1155 cm\(^{-1}\), and 1648 cm\(^{-1}\), associated with HPO\(_4\) antisymmetric stretching modes, and at 3275 cm\(^{-1}\), corresponding to water stretching vibrations, can be observed in this spectrum.

In the spectrum of the pure crystal, the most intense Raman line is observed at 987 cm\(^{-1}\), which is ascribed to the symmetric stretching vibrations of the phosphate (PO\(_4^4\)). In this case, this vibration band is situated at a higher energy than expected because for struvite material it is typically observed at 942 cm\(^{-1}\). Its position at a higher energy (987 cm\(^{-1}\)) indicates the formation of hydrogen phosphate units (HPO\(_4\)), which are characteristic of newberyite crystals [203]. The vibration bands at 3373 cm\(^{-1}\) and 3487 cm\(^{-1}\) are ascribed to POH stretching bands. Typically these vibrational lines are not observed in a struvite Raman spectrum. Hence, existence of these vibrational lines certainly substantiates the newberyite structure of the crystals. These lines are consequences of a strongly distorted newberyite orthorhombic structure, as compared to that of struvite. The characteristic bands at 409 cm\(^{-1}\), 501 cm\(^{-1}\), and 887 cm\(^{-1}\) are attributed to the HPO\(_4\) bending motion. Similar assignments of other features reveal that the features at 1056 cm\(^{-1}\), 1155 cm\(^{-1}\), and 1648 cm\(^{-1}\) are associated with HPO\(_4\) antisymmetric stretching modes and the features at 3275 cm\(^{-1}\) are attributed to water stretching vibrations, as can be observed in this spectrum.

From Figure 5.2 it can be seen that the main peaks observed in the spectra of the crystal with inhibitor definitely match those of newberyite. However, these features are not as finely delineated as in the Raman spectrum of the pure crystal. Furthermore, it can also be noticed that the vibrational band situated at 409 cm\(^{-1}\) does not exhibit any change in its position in either of the spectra. However, the vibrational bands at 501 cm\(^{-1}\), 887 cm\(^{-1}\), and 987 cm\(^{-1}\) are observed to exhibit shifting behavior toward higher wavenumbers. These vibrational bands are attributed to
the vibrations of phosphate (PO$_4$) units. Specifically about 46 cm$^{-1}$, 39 cm$^{-1}$, and 17 cm$^{-1}$ increases are observed in the positions of vibrational bands situated at 501 cm$^{-1}$, 887 cm$^{-1}$, and 987 cm$^{-1}$, respectively. These shifts to higher wavenumbers provide a strong indication of the possibility of chemical interaction between the crystal and inhibitor. This shifting behavior indicates chemical interaction between the crystal and inhibitor, through the oxygen of the phosphate units of newberyite. In addition, the spectra demonstrate the existence of new broad bands in the 2000 cm$^{-1}$, 2600 cm$^{-1}$, and 2800 cm$^{-1}$ region. These broad bands might be due to the RAL plant’s organic components.

5.4 Fourier Transform Infrared (FT-IR) Spectroscopic Characterization

In order to obtain further information about pure and inhibitor incorporated crystals we decided to perform infrared absorption spectroscopic characterizations, which require little sample preparation. The sample preparation includes sample grinding and mixing with a transparent CsI matrix prior to making pellets. However, since certain constituents might change during the grinding process and it might affect the results, powdering of the stone sample for infrared analysis is neither a good idea nor desirable. This might be an explanation of the absence of any perceptible differences between the spectra of the crystals without and with RAL inhibitor presented in Figure 5.3. In order to verify our assumption, we embedded the 2% RAL integrated sample i.e. with the highest inhibitor concentration, in a CsI matrix without any prior grinding. Surprisingly, no vibrations were obtained from the sample. The absolute absence of vibrational bands indicates the presence of a very strong reflecting component from the inhibitor.

After this we performed the experiment on a ground sample. In this case, typical newberyite vibrational lines at 897 cm$^{-1}$, 1022 cm$^{-1}$, 1063 cm$^{-1}$, 1167 cm$^{-1}$, 1240 cm$^{-1}$, 1654 cm$^{-1}$,
1712 cm$^{-1}$, 3483 cm$^{-1}$, and 3520 cm$^{-1}$ were observed [203 - 204]. In conclusion, the infrared spectra of the un-powdered sample revealed the strong reflecting nature of the inhibitor component and the infrared spectra of the powdered sample demonstrated the appearance of various newberyite vibrational bands.

**Figure 5.3:** Transmission measurements of crystals without and with 2% inhibitor, as labeled.
5.5 X-ray Photoelectron Spectroscopic (XPS) Characterization

From infrared characterization it was proved that the inhibitor exhibits a strong reflecting component. Beyond this finding, we were interested to discover the type of component responsible for the reflecting nature of the inhibitor. Hence, in order to ascertain which RAL component produced the reflecting behavior observed in infrared studies, an elemental analysis by X-ray photoelectron spectroscopy was performed. Initially, XPS survey scans were acquired for the crystals without and with 1% inhibitor with a view towards observing all peaks in the binding energy range from 0 to 1100 eV. The XPS survey scan spectra for the crystals without and with 1% inhibitor are shown in Figure 5.4.

From Figure 5.4, we can observe that there is an obvious difference between these spectra. As we can see, the main difference is the appearance of two dominant peaks at 1021.5 eV and 1044.6 eV in the spectra of crystal with 1% RAL inhibitor. These peaks are attributed to the binding energies of the Zn doublet lines $2p_{3/2}$ and $2p_{1/2}$, respectively [205].

The presence of Zn, indeed, not only can explain the reflecting phenomenon of the incident light in the infrared transmission measurements but also the inhibition of larger crystal growth. Studies of calculi composition propose that the existence of excessive quantities of elements such as zinc, iron, and copper in a local urine environment may initiate rapid stone formation [206]. Moreover, a foreign body insertion method using a zinc disc was employed in albino rats for inducing the growth of magnesium ammonium phosphate type stones [207-208]. For animals treated with this compound, a significant decrease in urinary stones was observed. The rapid stone crystallization may also induce the precipitation of other zinc compound, which may be the reason for the black color of the crystals with inhibitor.
Figure 5.4: XPS survey scans for the crystals without and with 1% inhibitor in the binding energy range from 0 to 1100 eV.

Furthermore, we also estimated the crystal ionicity by considering the chemical shifts of its key elements. Hence, afterward, with the help of the multiplex mode of the system control software, we examined the Zn $2p_{3/2}$, P 2p, Mg 2s, O 1s, N 1s and C 1s peaks in more detail. The resultant spectra are displayed in Figure 5.5 (a) – (f), respectively.
Figure 5.5: XPS spectra of: (a) Zn 2p$_{3/2}$; (b) P 2p; (c) Mg 2s; (d) O 1s; (e) N 1s; and (f) C 1s, the key elements. In all graphs the bottom spectrum is that of the pure crystal and the top spectrum is that of the crystal with 1% inhibitor.
From Figure 5.5 (a) it is clearly seen that there is no evidence of metallic zinc for the pure crystal. Moreover, it can also be noticed that for the crystal with inhibitor, the zinc peak is positioned at 1021.5 eV; which is exactly the same as the reported elemental zinc binding energy position [205]. Thus, there is no energy shift observed for the crystal with inhibitor.

In Figure 5.5 (b), the 132.5 eV characteristic binding energy of P 2p in a phosphate (PO₄) moiety is observed for the standard crystal. The figure also indicates that the addition of RAL herbal extract gives rise to different binding states for phosphorus. It demonstrates an increase, broadening, and a 3 eV higher energy shift of this line in the spectrum of the crystal with inhibitor. In fact, the reason for the broadening of this peak is the convolution of three spectral lines. Their presences are marked by arrows in Figure 5.5 (b). These lines can be easily illustrated as two shoulders at lower/higher energies with respect to the main line, which is centered at 135.5 eV and is attributed to different phosphorus oxidation states (e.g. P₂O₅) [205]. Comparison with the XPS standard crystal spectrum confirms that the lower energy shoulder coincides with the phosphorus oxidation state of PO₄ groups. The origin of the higher energy shoulder at approximately 140 eV is the contribution of the Zn 3s binding energy [205].

In Figure 5.5 (c), the Mg spectra have been plotted for samples without and with 1% LAR herbal extract and they indicate the presence of magnesium in both types of crystals. However, a significant increase in the intensity of the magnesium line is observed in Figure 5.5 (c) with the addition of the herbal extract. Hence, from these results it can be concluded that the inhibitor chemical composition contains a substantial amount of Mg. Besides this, from spectra it can be noticed that the spectrum of the pure crystal exhibits a 88eV Mg binding energy, which is characteristic of the Mg 2s oxidation state. Whereas, the spectrum of the herbal extract treated crystal exhibits a 86eV Mg binding energy. Thus, a 2 eV decrease in Mg binding energy is
observed between these two spectra of the crystals without and with herbal extract inhibitor, respectively.

In Figure 5.5 (d), spectra for oxygen have been presented, which demonstrate similar behavior to that previously presented for magnesium. In the spectrum of the crystal without RAL inhibitor, we assigned the 531 eV binding energy to undisturbed or nearly undisturbed oxygen states, i.e. surface adsorbed oxygen. On the other hand, in the spectrum of the crystal with RAL inhibitor, the slight shift of oxygen states to 529.6 eV is observed, which is quite in concurrence with the above Mg peak shift. This shift of oxygen states suggests the possibility of bonding between an oxygen site on the standard crystal surface and the Mg of the organic inhibitor [205, 209-210]. Moreover, the previously discussed possibility of modified phosphorus oxidation states (135.5 eV binding energy) might make a contribution as well. The confirmation for the assumption of possible Mg-O binding is also obtained from the Raman spectra. The Raman spectra of Figure 5.2 suggest that not only the presence of the of the 920 cm\(^{-1}\) and 1007 cm\(^{-1}\) peaks, but also the weak shoulder at 1112 cm\(^{-1}\) could be associated with this binding between magnesium from the inhibitor and oxygen from the phosphate units (PO\(_4\)) of the crystal.

In Figure 5.5 (e), we have presented the spectra of N for both types of crystals- without and with 1% LAR herbal extract. From the spectra it can be noticed that they are identical and the N 1s line of low intensity is centered at 396.9 eV in both spectra. In short, we do not observe any visible change for the N 1s line with inhibitor addition, which is more likely due to nitrogen’s interaction with magnesium. The existence of this line implies a struvite crystal structure. However, it’s very low intensity corroborates with the prevalence of a newberyite structure, as suggested previously.
The carbon peak at 282 eV is presented in Figure 5.5 (f). Generally, the reason for the appearance of the carbon peak is the unavoidable contact of the sample with air. From the spectra it can be observed that the carbon peak appears in both spectra. However, no changes are observed for this line, either.

5.6 Photoluminescence (PL) Spectroscopic Characterization

Finally, we also performed the photoluminescence spectroscopic characterization of the crystals with a view towards obtaining more insights and corroborating precisely our results achieved with the above analytical tools. In Figure 5.6, we have presented the photoluminescence spectra for the crystals grown without and with 1% and 2% RAL inhibitor.

The photoluminescence spectra reveal the maxima of the 580 nm peaks for the crystals grown without inhibitor and the dominant maxima of the 710 nm peaks for the crystals with inhibitor. Thus, the spectra indicate a redshift of about 130 nm. Since the pure crystal exhibits a whitish-transparent look, the photoluminescence from this crystal in the yellow range is quite comprehensible. Although, the photoluminescence from the pure crystal in the yellow range is reasonable, the striking similarity of the second peak to in vivo chlorophyll a photoluminescence deserves attention [211].

The reddish color of the reflected light observed in these experiments, previously called chlorophyll a photoluminescence, was investigated in detail by Song et al. in their laser-induced photoluminescence bio-applications [209]. However, the presence of a secondary peak at 735 nm can be observed in the photoluminescence spectra of the crystals with RAL inhibitor. The origin of this peak might be due to other organic compounds in the plant, which might fluoresce in the same range. From Figure 5.6, it can also be noticed that as the concentration of inhibitor
increases, the intensity of both the 710 nm and the 735 nm peaks increases, which is also quite sensible. Furthermore, since magnesium is a fundamental element of chlorophyll, the photoluminescence data are in excellent conformity with the XPS measurements, where a dramatic increase of this element was observed with inhibitor addition.

Figure 6: Photoluminescence spectra of crystals without and with 1% and 2% inhibitor, as labeled.
5.7 Concluding Remarks

In the present investigation we have carried out detailed multi-technique spectroscopic characterization of urinary calculi inhibition by RAL plant extract. In this complex process the influence of the binding between the magnesium from the inhibitor and the oxygen from the phosphate units of the standard kidney stone crystal is revealed by the spectroscopic analysis. Both, Raman and infrared absorption, reveal a newberryite structure for the crystal grown alone and with RAL inhibitor. Moreover, the presence of metallic Zn in the XPS measurements of the crystal with inhibitor is also likely to make an important contribution to the inhibition process. Rapid stone formation was reported for an excess amount of Zn in the local environment of calculi formation [206].

Also, the presence of Zn can explain the observed reflection of the incident light in the infrared transmission measurements for the unground crystals. No evidence of binding is depicted in XPS, Raman, and infrared absorption data for zinc. The photoluminescence results for the crystals with RAL inhibitor are similar to those of in vivo chlorophyll a photoluminescence [211]. Since, the presence of magnesium is expected in chlorophyll, the photoluminescence results corroborate with the XPS data, where an increase in the line intensity of this element is observed for the crystal grown with inhibitor.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

In the first phase of the present investigation, we have carried out detailed study of the hybrid organic-inorganic (or semi-organic) non linear optical material L-arginine doped potassium dihydrogen phosphate (KDP) crystal. In this examination we have performed comprehensive spectroscopic characterizations of pure and L-arginine doped KDP crystals in order to understand the interaction taking place between the L-arginine and KDP. Additionally, we have also performed thermogravimetric analysis in order to investigate the thermal effect of L-arginine doping on KDP.

In the second phase of the present exploration, an attempt was made to understand the effect of herbal medicine on the growth and inhibition of kidney stones by employing a systematic scientific study. We have adopted a multi-technique characterization approach to study the growth and inhibition of calculi based on a traditional medicine approach with herbal extracts.

Our conclusions for the present investigation as well as recommendations for future work for both phases are described below.

6.1 L-arginine Doped Potassium Dihydrogen Phosphate (KDP) Crystals

As noted above, in the present investigation an attempt was made achieve detailed characterizations of such organic-inorganic composite NLO materials based on amino-acid (L-arginine) doped Potassium Dihydrogen Phosphate (KDP) crystals.
In the present study, pure and 0.3 wt%, 0.4 wt%, as well as 0.5 wt% L-arginine doped KDP crystals were grown using solution growth techniques and further subjected to infrared (IR) absorption and Raman studies for confirmation of chemical group functionalization and for investigating the incorporation mechanism of the L-arginine organic material into the KDP crystal structure. With the help of Gaussian software, a prediction of possible incorporation mechanisms of the organic material was obtained from comparison of the simulated infrared and Raman vibrational spectra with the experimental results. Moreover, we also carried out the Thermo gravimetric analysis (TGA) in order to study the effect of L-arginine doping on thermal stability of the grown KDP crystal.

Infrared absorption spectroscopic analysis suggests that the spectra for 0.3 wt%, 0.4 wt% as well as for 0.5 wt% L-arginine doped KDP crystals are identical, except for a slight peak intensity difference. As the concentration of L-arginine doping increases, the vibrational peaks become more and more intense.

The infrared transmission data of standard and doped KDP crystals in the 400 – 2000 cm\(^{-1}\) range reveal that the main absorption bands at 537 cm\(^{-1}\), 900 cm\(^{-1}\), 1098 cm\(^{-1}\), 1297 cm\(^{-1}\), and 1677 cm\(^{-1}\) are characteristic of the KDP crystal. However, besides the main characteristic peaks of KDP, several extra peaks such as 1401 cm\(^{-1}\), 1637 cm\(^{-1}\), and 1716 cm\(^{-1}\) can be observed in the spectra of L-arginine doped KDP crystals. The occurrence of these additional vibrational lines is direct evidence of successful L-arginine doping.

The infrared spectrum of L-arginine doped material in the 2200-4000 cm\(^{-1}\) region does not simply reveal the vibrations related to KDP, but also demonstrates other very weak vibrations at 2854, 2925, and 3008 cm\(^{-1}\) which are associated with the CH\(_2\) lines of L-arginine at 2864, 2948, and 3070 cm\(^{-1}\) and shifted toward the lower energies by 10, 23 and 62 cm\(^{-1}\),
respectively. Moreover, apparently another vibrational line at 3127 cm\(^{-1}\) can be observed in the spectrum of KDP with 0.5 wt% L-arginine. The occurrence of the vibrational line at 3127 cm\(^{-1}\) in the spectrum of KDP with 0.5 wt% L-arginine is particularly noteworthy since it is attributed to a combination of N-H vibrations from NH\(_2\) and NH\(_3^+\) bands around the 3300 cm\(^{-1}\) region that are also downshifted to a lower energy.

Briefly, infrared spectroscopic analysis suggests that structural changes are proceeding for the L-arginine molecule as a result of its interaction with the KDP crystal. Infrared spectroscopic technique confirms disturbance of the N-H, C-H and C-N bonds of the amino acid, suggesting successful incorporation of L-arginine into the KDP crystals.

In Raman spectroscopic characterization, the standard KDP spectrum was recorded without any difficulties; different spectra were obtained for different spots on a single doped KDP crystal, suggesting a strong inhomogeneous doping.

The L-arginine Raman spectrum in the 300 – 1600 cm\(^{-1}\) region shows a multitude of vibrational lines, lines associated with vibrations of amino and carboxylate groups. The vibrational lines at 363, 474, 549, and 916 cm\(^{-1}\) are attributed to the phosphate bands of KDP. Among these phosphate peaks, the 363, 474, and 916 cm\(^{-1}\) peaks do not show any significant changes in their positions; however, a shift by approximately 19 cm\(^{-1}\) towards lower frequency is observed for the maximum of the broad line at 549 cm\(^{-1}\). This maximum position might be influenced by the existence in this frequency range of L-arginine C-skeleton bands at 554 and 619 cm\(^{-1}\). Additionally, various changes are observed for L-arginine vibrations in the 800 – 1500 cm\(^{-1}\) region.

Although the KDP material is undistinguished in the higher wavenumber region, there a multitude of L-arginine bands can be observed because of the C-H stretching of CH and CH\(_2\)
groups (around 2900 cm\(^{-1}\)) and N-H vibrations of NH, NH\(_2\), and NH\(_3^+\) (around 3300 cm\(^{-1}\)). The vanishing of L-arginine asymmetric NH and NH\(_2\) vibrations of the amino and guanidyl groups at 3296 and 3371 cm\(^{-1}\) were observed in the Raman spectrum of the amino-acid doped crystal. Moreover, the splitting evidence of the C-H bonding peaks at 2860 cm\(^{-1}\), 2924 cm\(^{-1}\), and 2950 cm\(^{-1}\) into peaks at 2838 cm\(^{-1}\), 2883 cm\(^{-1}\), 2908 cm\(^{-1}\), 2924 cm\(^{-1}\), and 2963 cm\(^{-1}\) can be observed. Taken together, the above considerations lead us to the possibility of an interpretation in terms of hydrogen bonding between the organic amino-acid and the inorganic material. Our conclusion allows for two different possibilities, in which energetic rearrangements of the L-arginine molecule occur as a result of the possible hydrogen bonding configurations between the nucleophilic O\(^-\) of the phosphate units of KDP and the NH\(_3^+\) groups of L-arginine.

In summary, Raman spectroscopic analysis also indicates that structural changes are taking place for the L-arginine molecule due to its interaction with the KDP crystal. Furthermore, Raman analysis also reveal disruption of the N-H, C-H and C-N bonds of the amino acid, implying successful inclusion of L-arginine into the KDP crystals.

Concisely, infrared transmission data and Raman characterization data are in good agreement. Both characterization techniques not only provide confirmation for the structural changes but also for the successful merger of L-arginine into KDP. However, only a qualitative study was performed for the crystals, due to the limitation arising from the strong inhomogeneity of the doped samples, which were synthesized using slow solvent evaporation growth techniques.

A possible model of hydrogen bonding between the oxygen of the KDP phosphate units and the NH\(_3^+\) groups of the amino-acid has been suggested here. This model was chosen as one of the simplest possibilities for accounting for the observed differences between infrared
absorption and Raman spectra of the L-arginine doped sample as compared with the standard samples. The inherent complexity and the likely inhomogeneity of the doped sample presently preclude proposing that this model is a unique and necessary explanation for the data obtained to date. Possible future work towards placing greater constraints on the plausible sample structures for explaining the spectra might include crystallizing KDP doped with amino acids of simpler structure (for example, alanine) to see which, if any, of the same or similar features appear in the spectra of the doped sample. We would expect such a comparison to provide further useful insight into this complex question.

Thermogravimetric analysis suggests that the pure KDP crystal is thermally stable up to 210°C in air atmosphere, the point where the dehydration process occurs. A 3% weight loss was observed between 210°C and 240°C due to the evaporation of the constitutional liquid (water) on the crystal surface. Beyond 285°C, thermal decomposition starts in the interior of the sample. The total weight loss for pure KDP crystals was around 11.65%, a loss that corresponds roughly to elimination of one water molecule for every KPO$_3$ unit. Therefore, initially, the crystal looses water of hydration, becoming anhydrous and remaining in that form up to the end of the analysis. Also, a large end residue was observed, which might be attributed to phosphate products.

A similar starting dehydration temperature of about 210°C was observed for L-arginine doped crystals. However, slightly increased liquid (water) weight losses were observed with different doping concentrations. These slight increases in the weight losses might be associated with the additional exclusion of NH$_3$ from L-arginine molecules. Beyond 285°C, the L-arginine doped KDP crystals also demonstrated major weight losses from decomposition of the main carbon chains, which will ultimately result in the formation of carbon dioxide.
On the whole, the L-arginine doped KDP crystals exhibited greater weight loss as compared to that of pure KDP, namely, a 12.63 wt%, a 14.48 wt% and a 16.19 wt% for 0.3 wt%, 0.4 wt%, and 0.5 wt% L-arginine doped crystals, respectively. Additionally, with increasing doping these weight losses not only occur at lower temperatures (of about 18°C lower) but also more rapidly. This observation suggests that an increasing level of L-arginine doping speeds the decomposition process and it weakens the KDP crystal, as expected, since amino acids become unstable at lower temperature. This observation indirectly provided evidence for the successful doping of the KDP crystals with L-arginine.

6.2 Growth and inhibition of calculi stone based on a traditional medicine approach with herbal extracts.

In the present investigation, we have also carried out a detailed scientific study of kidney stone formation and growth inhibition based on a traditional medicine approach with herbal extracts.

The complexity of calculi formation (i.e. nucleation, transformation, and aggregation) in a natural system such as urine was simulated to a certain extent in the present study by using a simplified single diffusion gel growth technique. The ammonium magnesium phosphate hydrate crystals were synthesized in a static gel environment without and with the presence of 1% and 2% concentrations of Rotula Aquatica Lour (RAL) herbal extracts. These grown crystals were characterized in order to analyze the effects of RAL on the growth of manganese-based calculi.

We expected to grow ammonium magnesium phosphate hexahydrate (\(\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}\)), or struvite crystals, as a result of the employed growth procedure. Normally, struvite crystals possess various morphological forms such as coffin, wedge-shape prism, and
needles. However, the crystals grown in the present study do not exhibit such forms, and, supported by a comparison with the comprehensive study of the formation and transformation of struvites and newberyites by Babic-Ivancic et al. [220], we conclude that the products of the current work are more likely newberyites.

Moreover, observation of the crystals indicates that there are drastic changes in size, color, and shape of the RAL incorporated calculi crystals. It was observed that as the amount of RAL inhibitor increases, the crystal sizes decrease. Moreover, when RAL inhibitor was used, not only was a dramatic decrease in crystal size observed, but also a noticeable color change was observed, from a white-transparent pure crystal to black-opaque crystals. This color change is a clear indication of chemical interactions between the crystal and the inhibitor’s organic molecules. However, if segmented or crushed, the crystal’s interior is again white-transparent. Thus, the plant inhibitor directly contributes to impeding the growing process by passivating the crystal surface and forming a surface compound.

In the Raman spectra, there was a noticeable increase in the Raman scattering background for the crystals with RAL; particularly in the Raman spectrum of the crystal with 2% RAL. This scattering, originating from the inhibitor’s extremely high fluorescence, imposes the need for linear photoluminescence background subtraction, which was performed for such spectra. This substantially increased scattering unfortunately obstructed obtaining good quality Raman data. Besides this striking scattering background increase, no notable difference was observed with increasing inhibitor concentration.

The most intense Raman line at 987 cm\(^{-1}\) in the spectrum of the pure crystal was attributed to the symmetric stretching vibrations of the phosphate units (PO\(_4\)). For the expected struvite crystals this line was assumed to occur at 942 cm\(^{-1}\). Thus, its position at a higher energy
than that expected for the struvite material indicates the formation of hydrogen phosphate units (HPO$_4$), which are characteristic of newberyite crystals [221]. Furthermore, the existence of peaks at 3373 cm$^{-1}$ and 3487 cm$^{-1}$, assigned to POH stretching bands, also confirm the newberyite structure of the crystals because these vibrations typically are absent in a struvite Raman spectrum. These lines are consequences of a strongly distorted newberyite orthorhombic structure, as compared to that of struvite.

The main peaks in the spectra of the crystals with inhibitor essentially matched those of newberyite; however, this mineral is not as clearly identified as in the Raman spectrum of the pure crystal. There are clear shifts to higher energy for other vibrational bands; about 46 cm$^{-1}$, 39 cm$^{-1}$, and 17 cm$^{-1}$ increases were observed in the positions of the phosphate unit (PO$_4$) vibrations at 501 cm$^{-1}$, 887 cm$^{-1}$, and 987 cm$^{-1}$, respectively. These shifts to higher wavenumbers can possibly be due to chemical interaction between the crystal and inhibitor, through the oxygen of the phosphate units of newberyite. In addition, the spectra have shown the existence of new broad bands in the 2000 cm$^{-1}$, 2600 cm$^{-1}$, and 2800 cm$^{-1}$ region, likely due to the RAL plant’s organic components.

In short, Raman spectroscopy clearly provided an indication of the newberyite type of crystal as well as shedding light on the chemical interaction between crystal and inhibitor. Moreover, it also indicated the presence of organic components due to the RAL plant material.

In the infrared spectra of the sample with the highest inhibitor concentration i.e. 2% RAL, embedded in a CsI matrix without any prior grinding, no vibrational lines were observed. Hence, the infrared spectra suggest the existence of a strongly reflecting component in the inhibitor. However, after grinding, infrared spectra also revealed the existence of typical newberyite
vibrational lines such as those at 897 cm\(^{-1}\), 1022 cm\(^{-1}\), 1063 cm\(^{-1}\), 1167 cm\(^{-1}\), 1240 cm\(^{-1}\), 1654 cm\(^{-1}\), 1712 cm\(^{-1}\), 3483 cm\(^{-1}\), and 3520 cm\(^{-1}\).

In short, infrared absorption spectroscopy not only indicated the presence of a strong reflecting component in the inhibitor but also the newberyite structure of crystal.

The XPS survey scans for the crystals with 1% inhibitor demonstrate the existence of two dominant peaks at 1021.5 eV and 1044.6 eV, attributed to the binding energies of the Zn doublet lines \(2p_{3/2}\) and \(2p_{1/2}\), respectively [222]. The presence of Zn can certainly account for the reflecting process of the incident light in the infrared transmission measurements, as well as the inhibition of larger crystal growth. Rapid stone crystallization may also induce the precipitation of other zinc compounds, which may be the reason for the black color of the crystals with inhibitor.

The careful examination of the Zn peak through the multiplex mode of the system control software clearly indicated the presence of metallic zinc in the crystal with inhibitor. Furthermore, it also indicated that there is no energy shift from the reported elemental zinc binding energy position of 1021.5 eV for the inhibitor incorporated crystal. Similar examination of phosphorus peaks revealed that the addition of RAL herbal extract gives rise to different binding states for phosphorus. A considerable increase in the intensity of the magnesium line was seen with the addition of the herbal extract, which suggests that the inhibitor chemical composition contains a substantial quantity of Mg. Moreover, the decrease in the Mg binding energy corresponding to the characteristic of Mg 2s oxidation state was observed for the crystal with inhibitor. Similar behavior was seen for the oxygen peak. Hence, in conjunction with the above Mg peak shift, the slight shift of the oxygen state to 529.6 eV suggests the possibility of bonding between an oxygen site on the standard crystal surface and the Mg of the organic inhibitor [222-224].
Additionally, the previously mentioned possibility of modified phosphorus oxidation states might make a contribution, too. The Raman spectrum also suggests possible Mg-O binding. No visible change was observed with inhibitor addition for the N 1s line centered at 396.9 eV, possibly due to nitrogen’s interaction with magnesium. Although the existence of this line implies a struvite crystal structure, its very low intensity corroborates with the prevalence of a newberyite structure, as previously suggested. The carbon peak at 282 eV was observed because of the unavoidable contact of the sample with air. However, no changes were observed for this line, either.

The photoluminescence spectra of the crystal with inhibitor indicated the presence of chlorophyll by exhibiting a dominant peak at 735 cm$^{-1}$. The intensity of this peak increased with the concentration of inhibitor. Also, since magnesium is a central component of chlorophyll, the photoluminescence data are in good agreement with the XPS measurements, where a dramatic increase of this element was observed with inhibitor addition. Furthermore, the presence of a secondary peak at 735 nm can be observed in the photoluminescence spectra of the crystals with RAL inhibitor. The origin of this peak might be due to other organic compounds in the plant, which might fluoresce in the same range.

In summary, detailed spectroscopic analysis of urinary calculi inhibition by RAL plant extract revealed the influence in this complex process of the binding between the magnesium from the inhibitor and the oxygen from the phosphate units of the standard kidney stone crystal. A newberyite structure for the crystal grown alone and with RAL inhibitor has been confirmed by both Raman and infrared absorption spectroscopy.

The presence of metallic Zn, as revealed in the XPS measurements of the crystal with inhibitor, is likely to make an important contribution to the inhibition process, too. Indeed, rapid
stone formation was reported in the literature for an excess amount of Zn in the local environment of calculi formation [225]. Also, the presence of Zn can explain the observed reflection of the incident light in the infrared transmission measurements for the unground crystals. Furthermore, the observed reflection of the incident light in the infrared transmission measurements for the unpowdered sample can be easily explained by the presence of Zn. XPS, Raman, and infrared data for zinc did not illustrate any evidence of binding. The photoluminescence results of the crystals with RAL inhibitor were similar to those of in vivo chlorophyll a photoluminescence [226]. Since the presence of magnesium is expected in chlorophyll, the photoluminescence results corroborate with the XPS data, where an increase in the line intensity of this element was observed for the crystal grown with inhibitor.

In conclusion, our present exploration was provided evidence of Mg- and Zn-related inhibition of urinary calculi formation with the addition of RAL herbal extract, contributing, from the spectroscopic point of view, to an intricate subject. We thus assume that our research work will serve as an important source of information on this tantalizing and multifaceted problem, which is not completely understood so far.
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166


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Curriculum Vitae

Jayesh Govani, son of Mrs. Indumati Govani and Mr. Rasiklal Govani, was born in Dhrangadhra, Gujarat, India. He enrolled at the M. P. Shah Arts and Science College, India in 1987, where he earned his Bachelors degree. He earned his Master’s degree in Physics from Saurashtra University, India followed by eminent Master’s of Philosophy degree in July 2003. He achieved First Class with Distinction in Master of Philosophy program. He joined as a Lecturer in Physics at M. P. Shah Arts and Science College, Surendranagar, India in Nov, 1993 and he served as lecturer until July, 2005. He commenced his journey towards Doctoral program at University of Texas at El Paso in Material Science & Engineering from August 2006.

Dr. Govani has been recipient of multiple exemplary awards during his academic phase at University of Texas at El Paso prominently Cotton Memorial Graduate Scholarship award, Roy and Keith Chapman Graduate Scholarship award, Dodson Research Fellowship and Jhamandas Watumall Fund Scholarship award.

During his doctoral studies at UTEP, Dr. Govani has served as graduate teaching and research assistant effectively fulfilling responsibilities of position and justifying the faith reposed in him by the institution. He has credible research publications prominently in arena of spectroscopic study of different materials of various fields such as L-arginine doped KDP crystal, inhibition of urinary calculi and dye-mineral composites published in Journal of Raman Spectroscopy and Journal of Materials Research. He has presented multiple presentations on his research findings prominently at American Physics Society and Joint Texas section meeting of APS, AAPT and Zone 13 of SPS.

Dr. Jayesh Govani’s dissertation entitled “Spectroscopic characterizations of organic/inorganic nanocomposites” was supervised by Dr. Felicia Manciu.