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# Growth and Characterization of L-Alanine Crystals using FT-IR, UV Visible Spectra

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**Abstract:** ***The L-alanine family crystals such as pure L-Alanine, hydrochloride (HCl) mixed L- alanine, potassiumchloride (kcl) mixed l-alanine and potassium dihydrogen phosphate (kdp) mixed l-alanine have been successfully grown from the aqueous solution by slow evaporation method at room temperature. The grown crystals FT-IR spectral studies were recorded for each sample and the molecular vibrational frequencies confirmed with the standard frequencies. The optical transparency was found out for each crystal by recording the UV-Visible spectrum.***

**Keywords:** UV, FT-IR, L. Alanine, Vibrational energy, dipole moment

## 1. Introduction

The degree of purity and perfection of crystals are to be known to interpret the structure dependent properties in order to determine whether the material can be successfully employed in the experiments or in the device fabrication process. It is also important to know the nature and distribution of the imperfections present in the crystals. A thorough assessment can only determine the quality and perfection of the crystals and their properties.

Detailed studies of the crystals can provide clues to deduce how the growth techniques should be modified so that the perfection of the crystal may be increased. Characterization of a crystal essentially consists of its chemical composition, structure, defects and the study of their electrical, mechanical and optical properties. The study of the growth defects includes the defects such as inclusions, step growth, mechanical stress etc., which result due to poor control of crystal growth parameters.

In the field of nonlinear optical crystal growth, amino acids are playing a vital role. Many numbers of natural amino acids are individually exhibiting the nonlinear optical properties because they have a donor $NH_2^+$ and acceptor $COOH^-$ and also intermolecular charge transfer is possible. Especially natural amino acids of aspartic and glutamic and as well as Arginine, Lysine, L-Alanine and Y-glycine are evidently showing NLO activity because of an additional COOH group in the first and $NH_2$ group in the second. Also, some of the amino acids are used as dopants and they enhance the material properties like Non linear optical and ferroelectric properties. A series of semi-organic compounds such as L-Alanine, L-Arginine diphosphate crystals have been reported with moderately high mechanical and chemical stability.

## 2. Property and structure of L-alanine

The structure of L – Alanine has been solved by West (1930) and it was later confirmed by Frazer and Pepinsky (by X-ray diffraction studies) and Bawn and Pease (by neutron diffraction studies). L-alanine belongs to the space group is $P2_1, 2_1, 2_1$. The unit cell dimensions are a = 6.023Å b= 12.343 Å, C = 5.784 Å; α= β= γ= 90° obtained from the analysis are given in the table-1

**Table 1:** Crystallographic Data of L–Alanine

| *Chemical Formula* | *$CH_3CHNH_2COOH$* |
|---|---|
| Molecular Weight | 89.09 |
| Space group | $P2_12_12_1$ |
| A | 6.023 Å |
| B | 12.343 Å |
| C | 5.784 Å |
| α= β= γ | 90° |

- Member of amino acids
- Strongest basic amino acids
- Chemical formula $CH_3CHNH_2COOH$
- Orthorhombic crystal system
- Molecular weight is 89.1 gm
- Melts with decomposition of $297^0$ C
- High solubility in water and insoluble in diethyl ether
- Having 99% purity
- Appearance : White power
- Having high stability

### 2.1 Present Investigation

In the present work, pure crystals of L–Alanine, HCl, KCl and KDP mixed L Alanine crystals have been grown by slow evaporation method.

## 3. Materials and Methods

### 3.1 Ft-ir studies

FT-R (Fourier Transform Infrared) Spectroscopy is a technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FT-R analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks.

The resulting FT-R spectral pattern is then analyzed and matched with known signatures of identified materials in the FT-R library. The detailed insight into the nature of molecules can be studied by the absorption of radiation that result transition among the vibrational energy levels. Further FT-IR is an effective tool which provides information about the nature of bonding involved. In order to absorb infrared radiation a molecule must undergo a net change in dipole moment, as a consequence of its vibrational motion. Vibrational energy values are quantized and accessible region of infrared is from 4000-400cm$^{-1}$ for each vibrational state.

For organic molecules the IR spectrum can be divided into two regions. The two regions are functional group region and finger print region. The functional region occur in the region of 4000-1500 cm$^{-1}$ and their regional peaks are characteristics of specific kind of bonds and therefore can be used to identify whether a specific functional group is present. The finger print region occurs in the range 1500-1400 cm$^{-1}$. These regional peaks arise from complex deformation of the molecule. They may be characteristics of molecular symmetry or combination bands from multiple bonds deforming simultaneously.

### 3.2 To analyze the spectra

**Step 1:** Look first for carbonyl C=O bend. Look for a strong band at 1820 – 1660 cm$^{-1}$. This band usually is the most intense absorption band in a spectrum. It will have medium width. If we see the carbonyl band, look of other ands associated with functional groups that contain the carbonyl by going to step 2. If no C=O band is present, check for alcohols and go the step 3.

**Step 2:** If a C=O is present we want to determine if it is a part of an acid, an ester, or an aldehyde or ketone. At this time we may not able to distinguish aldehyde from ketone and you will not be asked to do so.

***Acid***: Look for indications that an O-H is also present. It has a broad absorption near 3300 – 2500 cm$^{-1}$. This actually will overlap the C-H stretch. There will also be a C-O single band near 1100 – 1300 cm$^{-1}$. Look for the carbonyl and band near 1725 – 1700 cm$^{-1}$.

***Ester:*** Look for C=O absorption of medium intensity near 1300 – 1000 cm$^{-1}$. There will be no O-H band.

***Aldehyde***: Look for aldehyde type C-H absorption bands. There are two weak absorptions to the right of the C-H stretch near 2850 cm$^{-1}$ and 2750 cm$^{-1}$ and are caused by the C-H band that is a part of the CHO aldehyde functional group. Look for the carbonyl C-O band around 1725 – 1705 cm$^{-1.}$

**Step 3:** If no carbonyl band appears in the spectrum looks for an alcohol O-H band.

***Alcohol:*** Look for the broad OH band near 3600 – 3300 cm$^{-1}$ and a C-O absorption band near 1300 – 1000 cm$^{-1}$.

**Step 4:** If no carbonyl band and no O-H bands are in the spectrum check for double bands, C=C from an aromatic or an alkene.

***Alkene:*** Look for weak absorption near 1650 cm$^{-1}$ for a double band. There will be a C-H stretch band near 3000 cm$^{-1}$.

***Aromatic:*** Look for the benzene C=C, double bonds which appear as medium to strong absorption in the region 1650 – 1450 cm$^{-1}$. The CH stretch bond is much weaker than in alkenes.

**Step 5:** If none of the previous groups can be divided, we may have an alkane.

***Alkane:*** The main absorption will be the C-H stretch near 3000 cm$^{-1}$. The spectrum will be simple with another band near 1450 cm$^{-1}$.

**Step 6:** If the spectrum still cannot assigned we may have an alkyl bromide.

***Alkyl bromide:*** Look for the C-H stretch and a relatively simple spectrum with an absorption to the right of 667 cm$^{-1}$. Absorption **Note:** Terminal C-$CH_2$:

at 1600 – 1675 cm$^{-1}$
Strong bands at 900 cm$^{-1}$.

Aromatic ring breathing motions: Observed between 1450 cm$^{-1}$ and 1600 cm$^{-1}$ the interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for types of bands.

**Table 2:** A model table is given below which is helpful for analyzing a FT-IR spectrum

| *Bond* | *Compounds,elements etc.,* | *Frequency Range* |
|---|---|---|
| O=H | Monomeric – Alcohols, phenols | 3640 – 3160 (s, br) |
| | Hydrogen bonded alcohols, phenols | 3600 – 3200 (b) stretch |
| | Carboxylic acids | 3000 – 3300 (m) stretch |
| N-H | Amines | 3500 – 3300 (m) bend |
| | | 1650 – 1580 (m) bend |
| C – N | Amines | 1340 – 1020 (m) stretch |
| C=N | Nitriles | 2260 – 2220 (v) stretch |
| $NO_2$ | Nitro compounds | 1660 – 1500 (s)<br>asymmetrical stretch |

V = Variable, m = Medium s – Strong W – weak sh - sharp

### 3.3 UV-visible spectra

Many molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length b, and the concentration c, of the absorbing species. Beer's law states that,

$$A = ebc$$

Where 'e' is the constant of proportionality called the absorbability.

Different molecules absorb radiation of different wavelengths. An absorption band corresponds to structural groups within the molecule. UV-Vis spectroscopy is the measurement of the wavelength and intensity of absorption of near-ultraviolet and visible light by a sample. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels. UV-Vis spectroscopy is usually applied to molecules and inorganic ions or complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer Lambert Law. The UV-Visible spectra give limited information about the structure of the molecules because the absorption of UV and visible light involves promotion of the electron in $\sigma$ and $\pi$ orbitals from the ground state to higher energy states.

For a nonlinear optical material, transmission spectra are very important to the nature of the material and material should possess wide transparency range. Moreover, damage is more likely to occur in the crystal when it absorbs the fundamental or harmonic wavelengths. Hence the NLO material should have high high damage threshold.

## 4. Growth procedure of pure L-Alanine crystals

### 4.1 Growth of Pure L- Alanine crystals

The starting material L-Alanine was dissolved in double distilled water and the saturated solution was filtered by micro filter paper. It was then covered with aluminum foil as a lid and made some holes on it for evaporation of the solvent. Keep on evaporation without disturbing the beaker the seed crystal grow and attained the maximum size till they get evaporated. Optical quality crystal of dimension 5 x 3 x1 mm$^3$ has been grown over typical growth period of 35 days. The grown crystals of L-Alanine crystal were shown in Fig-1

### 4.2 Growth of HCl mixed L-Alanine crystals

The HCl mixed L-Alanine was synthesized by taking 1:1 ratio of L-Alanine and Hydrochloric acid (HCl). The above ratio of the HCl and L-Alanine were mixed in 25 ml of double distilled water and maintained at 60 degree for about 5 hours and white powder of HCl mixed L-Alanine was formed. The synthesized salt was mixed in double distilled water till it get super saturated. The super saturated solution was kept for evaporation. Keep on evaporation without disturbing the beaker the seed crystal grown and attained the maximum size till the solvent get evaporated. Optical quality crystal of dimension 8 x 1 x 1 mm$^3$ has been grown over typical growth period of 30 days. As grown crystals of HCl mixed L-Alanine is shown in Fig-2

### 4.3 Growth of KDP mixed L Alanine crystals

The KDP mixed L-Alanine crystal was grown usual procedure as mentioned above by taking 1:2 ratio of L-Alanine and KDP. The reaction takes place in this process as follows. After 20 days the crystal has been grown. The grown crystals were having dimension of (8 x 1 x 1 mm$^3$).

The grown crystal is shown in the Fig-3

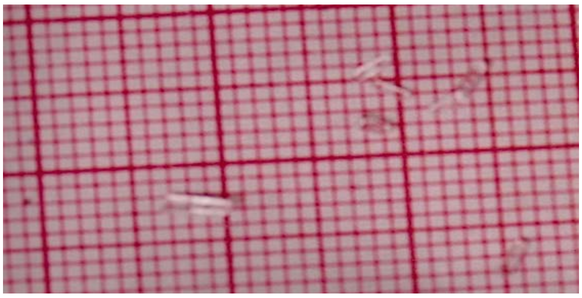

**Figure 1:** Grown crystal of pure L-Alanine crystals

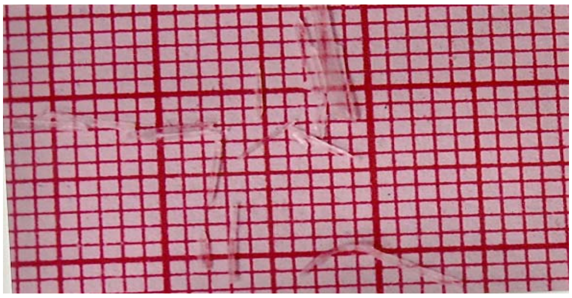

**Figure 2:** Grown crystal of HCl mixed L-Alanine crystals

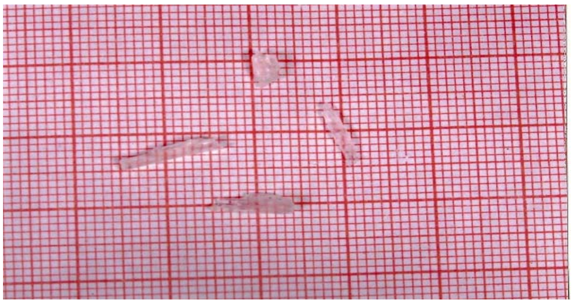

**Figure 3:** Grown crystal of KDP mixedL-Alanine crystals

## 5. Characterization of L-Alanine family crystals

### 5.1 FT-IR Spectral Studies

The FT-IR spectrum of Pure L-Alanine, HCl, KCl and KDP mixed L-Alanine crystals were recorded at room temperature using SPECTRUM RXI 213V FT-IR spectrometer. The four spectrums are shown in Fig-4, 5, 6, 7

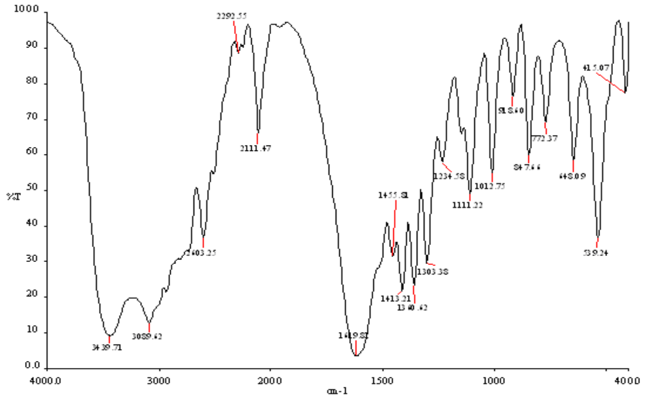

**Figure 4:** FT-IR spectrum of pure l-Alanine crystals

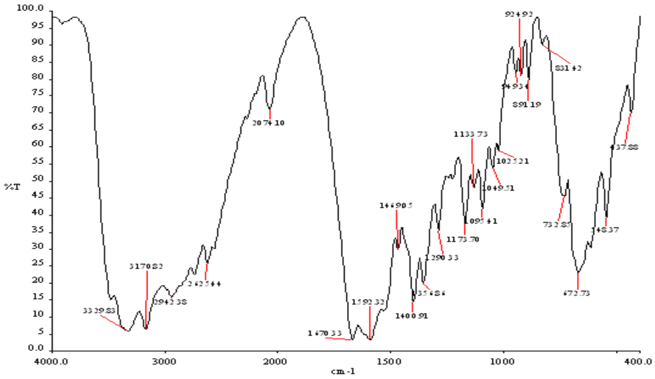

**Figure 5:** FT-IR spectrum of HCl mixed l-Alanine crystals

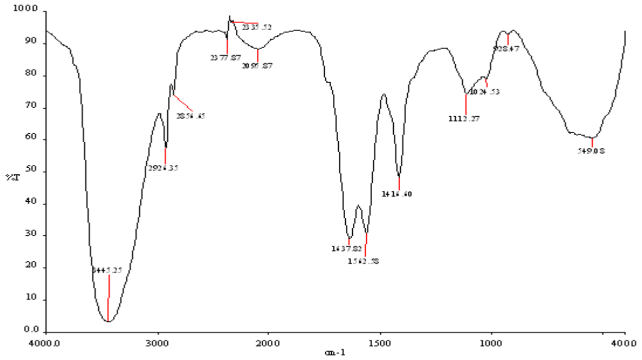

**Figure 6:** FT-IR spectrum of KCl mixed L-Alanine crystal

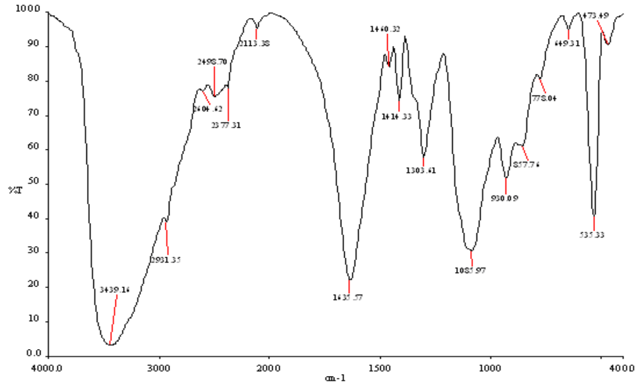

**Figure 7:** FT-IR spectrum of KDP mixed L-Alanine crystals

### 5.2 UV Spectral Studies

Optical transmission studies were recorded for the sample obtained from the crystal. The sample is prepared by dissolving the powder in the water. To find the transmission range of L-Alanine crystal the optical transmission spectrum was recorded using Varian carry 5E UV-Vis Nir spectrophotometer. In the wavelength range between 190 to 1100 nm. Optical transmission spectra of the above samples obtained from Lambda 35 UV spectrometer. It is shown in Fig-8, 9 and 10.

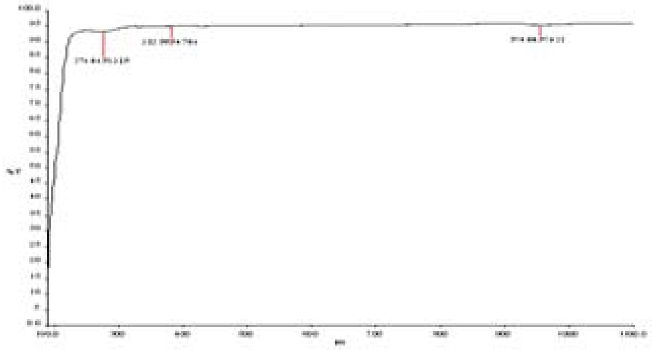

**Figure 8:** UV-Visible spectrum of pure L-Alanine crystals

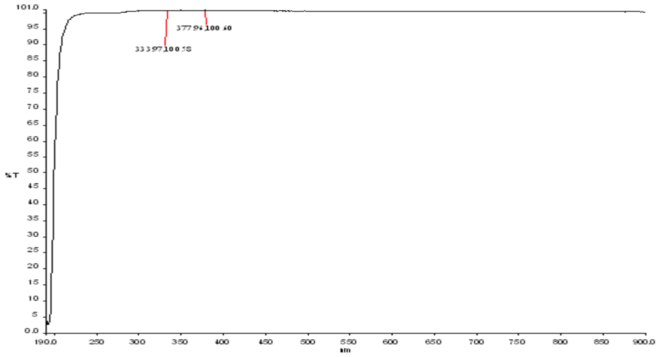

**Figure 9:** UV-Visible spectrum of KCl mixed L-Alanine crystals

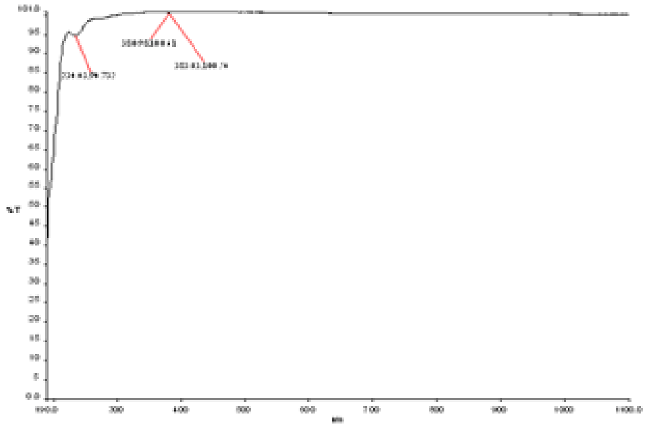

**Figure 10:** UV-Visible spectrum of KDP mixed L-Alanine crystal

## 6. Result and Discussion

**FT-IR spectral analysis**

**FT - IR spectral analysis of L - Alanine**

The frequency assignments for L-Alanine family crystals are listed in Table-3, 4, 5 and 6.

**Table 3:** Frequency assignments for Pure L-Alanine crystals

| *Frequency ($cm^{-1}$)* | *Nature of the Peak* | *Assignment* |
|---|---|---|
| 2603.25 | m | $CH_3$ sym. streching |
| 3089.62 | m | CH Stretching |
| 1619.81 | s | C=O stretching |
| 2292.55 | s | $NH_2$ asym. Stretching |
| 3439.71 | v | OH stretching |

- The medium intensity peaks obtained in the region 2603 $cm^{-1}$ corresponds to $CH_3$ symmetric Stretching vibration.
- The medium intensity peaks obtained in the region 3089 $cm^{-1}$ corresponds CH Stretching vibration.
- The strong intensity peaks obtained in the region 1619 $cm^{-1}$ corresponds C=O stretching vibration.
- The strong intensity peaks obtained in the region 2292 $cm^{-1}$ corresponds $NH_2$ asymmetric stretching vibration.
- The variable intensity peaks obtained in the region 3439 $cm^{-1}$ corresponds OH stretching vibration.

### 6.1 FT - IR spectral analysis of HCL mixed L – Alanine

**Table 4:** Frequency assignments for HCl mixed L-Alanine crystals

| *Frequency ($cm^{-1}$)* | *Nature of the Peak* | *Assignment* |
|---|---|---|
| 1413.06 | m | $CH_3$ sym. stretching |
| 3084.89 | w | CH Stretching |
| 1619.68 | s | C=O stretching |
| 2603.39 | s | $NH_2$ asym. Stretching |
| 3439.16 | v | O-H stretching |
| 774.40 | s | C-Cl stretching |

- The medium intensity peaks obtained in the region 1413 $cm^{-1}$ corresponds to $CH_3$ symmetric Stretching vibration.
- The weak intensity peaks obtained in the region 3084 $cm^{-1}$ corresponds CH Stretching vibration.
- The strong intensity peaks obtained in the region 1619 $cm^{-1}$ corresponds C=O stretching vibration.
- The strong intensity peaks obtained in the region 2603 $cm^{-1}$ corresponds $NH_2$ asymmetric stretching vibration.
- The variable intensity peaks obtained in the region 3439 $cm-^{1}$ corresponds OH stretching vibration.
- The strong intensity peaks obtained in the region 774 $cm^{-1}$ corresponds to C-Cl stretching.

### 6.2 FT - IR spectral analysis of KCL mixed L – Alanine

**Table 5:** Frequency assignments for KCl mixed L-Alanine crystals

| *Frequency ($cm^{-1}$)* | *Nature of the Peak* | *Assignment* |
|---|---|---|
| 2926.35 | m | $CH_3$ sym. Stretching |
| 1416.60 | s | CH Stretching |
| 1637.82 | s | C=O stretching |
| 2377.87 | s | $NH_2$ asym. Stretching |
| 549.08 | s | C-Cl stretching |
| 3445 | v | OH stretching |

- The medium intensity peaks obtained in the region 2926 $cm^{-1}$ corresponds to $CH_3$ symmetric Stretching vibration.
- The medium intensity peaks obtained in the region 1416 $cm^{-1}$ corresponds CH Stretching vibration.
- The strong intensity peaks obtained in the region 1637 $cm^{-1}$ corresponds C=O stretching vibration.
- The strong intensity peaks obtained in the region 2377 $cm^{-1}$ corresponds $NH_2$ asymmetric stretching vibration.
- The strong intensity peaks obtained in the region549 $cm^{-1}$ corresponds to C-Cl stretching.
- The variable intensity peaks obtained in the region 3445 $cm-^{1}$ corresponds OH stretching vibration.

### 6.3 FT - IR spectral analysis of KDP mixed L – Alanine

**Table 6:** Frequency assignments for KDP mixed L-Alanine Crystals

| *Frequency ($cm^{-1}$)* | *Nature of the Peak* | *Assignment* |
|---|---|---|
| 2931.35 | W | $CH_3$ sym. streching |
| 1414.33 | S | CH Stretching |
| 1635.57 | S | C=O stretching |
| 2604.62 | S | $NH_2$ asym. Stretching |
| 3439.16 | W | O-H stretching |
| 1303.61 | M | P=O stretching |
| 1035.97 | M | P-O stretching |

- The weak intensity peaks obtained in the region 2931 $cm^{-1}$ corresponds to $CH_3$ symmetric Stretching vibration.
- The strong intensity peaks obtained in the region 1414 $cm^{-1}$ corresponds CH Stretching vibration.
- The strong intensity peaks obtained in the region 1635 $cm^{-1}$ corresponds C=O stretching vibration.
- The strong intensity peaks obtained in the region 2604 $cm^{-1}$ corresponds $NH_2$ asymmetric stretching vibration.
- The weak intensity peaks obtained in the region 3439 $cm^{-1}$ corresponds to OH stretching.
- The medium intensity peaks obtained in the region 1303 $cm-^{1}$ corresponds P=O stretching vibration.
- The medium intensity peaks obtained in the region 1035 $cm^{-1}$ corresponds to P-O stretching vibration.

### 6.4 UV Spectral Analysis

The comparison of four spectra showed that the lower UV cutoff frequency for pure L-Alanine, HCl, KCl and KDP mixed L-Alanine crystals are more or less same and also show that mixing of HCl, KCl and KDP did not change the shift of lower cutoff value. From the graphs, it is clear that the optical transparency foun 93% for pure L-Alanine, 94% for HCl mixed L-Alanine, 100% for KCl mixed L-Alanine and 94% for KDP mixed L-Alanine crystals.

## 7. Conclusion

Good quality of L-Alanine, HCl, KCl, and KDP mixed L-Alanine crystals were grown by slow evaporation method. These crystals were characterized by FT-IR, UV visible spectrum. The FT-IR spectrum confirms the presence of molecules in grown crystals and the frequency assignments explain the nature of the bonding between them. From these studies, it is evident that the hydrogen bonding due to $NH_2^{\ +}$ and $COOH^-$ moieties is the additional major force in the crystal lattice. .Our results contribute to a better understanding of the interaction between amino acids and the acid complexes in the crystalline state.

The UV visible spectral analysis shows that the grown crystals have optical transparency above 90% and they are good optically transparent crystals. From the UV spectral analysis of the above crystals, HCL mixed L- Alanine has the maximum transparency. By using the transmittance spectrum, the absorption edge was observed below 300nm and it is concluded that the crystal can be used beyond this wavelength for device fabrications. It is an important requirement for the materials having NLO properties. From the above studies, it is concluded that the optical and mechanical properties of the crystals can be tuned as per our requirements.

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