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# Studies on Growth and Characterization of Single Crystal using L-Leucine, L-Phenylalanine and L-Valine in Aqueous medium of $KNO_3$ and Molecular interaction by exposing the Samples to Ultrasonic Frequency of 2MHz

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**Abstract:** The single crystals of LVKN, LLKN and LPKN were grown by slow evaporation technique. The crystalline nature and structures of mentioned crystals were confirm by X-ray diffraction analysis. FT-IR studies show the functional group of the material components. The good optical suitability was been confirmed through UV-Vis Spectrum. The encouraging crystal growth characteristics and their properties of titled crystals recommend it as a potential material for SHG device application.
**Keywords:** Crystal growth, UV-Vis spectrum, FT-IR Spectrum Powder diffraction, SHG.

## 1.0. Introduction

Most common issues regarding sound speed in solid, liquid and gases have been proved by the researchers form their past decades as sound travels very high in solid. Ultrasonic interferometer a wonderful device for seeking apparent molar compressibility, apparent molar volume and so on through the velocity of sound wave in liquid. Researchers have been attempted many trials to see what will ensue the velocity of sound waves travels in liquid media in different molar concentration and temperature modulation attempt (1). Amino acid components have most common biomolecular components and it contain intermolecular bonds, because of interaction between protein molecules and the solvent ions. To compare the speed of sound in 1.29 $E^{-6}$ $\Omega^{-1}$ specific conductive solution to Amino acid doped Solution, the speed of sound has been increased by imitable amount. The present research work has been done by using the amino acid components L-Valine, L-Leucine, and L-Phenylalanine which are doped with inorganic $KNO_3$ and investigate the material nature of the titled issues. At the same time this research work was modified and the same composition from the state of liquid into crystalline solid nature of the titled components through slow evaporation crystal growth technique. The optical and structural activities identify the characteristic nature of the material which helps to distinguish the solid and liquid nature of the titled components.

## 2.0. Experimental Method

The Apparent molar compressibility ($\varphi_k$) and apparent molar volume ($\varphi_v$) of L-valine, L-leucine and L-phenylalanine in aqueous solution of $KNO_3$ at different concentrations were determined at the temperature 303.15 K and the above parameters can be evaluated from precise density, ultrasonic velocity. With the help of these results various ultrasonic derived parameters such as limiting apparent molar compressibility ($\varphi_k^o$), limiting apparent molar volume ($\varphi_v^o$), and their constant ($S_k$, $S_v$), viscosity A & B-coefficients and the

corresponding transfer parameters ($\Delta\varphi_k^o$, $\Delta\varphi_v^o$ and $\Delta B$), were evaluated and reported in research paper (2)

Velocities of sound for various molecular compositions have been carried out by using ultrasonic interferometer. Region of middle and approximate molecular composition 0.5 and 1.0 KNO3 verses 0.05 L-Valine, L-Leucine and L-Phenylalanine were taken and crystallizes by slow evaporation techniques. The calculate amount was first dissolved in deionized water. The solution was agitated with a magnetic stirring device of 6h to 7h continuously and filtered after complete dissolution of the starting materials. The Prepare solution was left to standby for almost 30 days at the 300 K. colorless and rod shape crystals were obtained for various compositions as shown in fig.1.

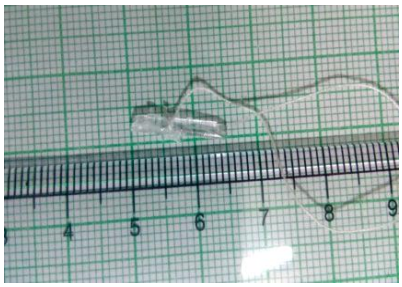


**Fig1a**

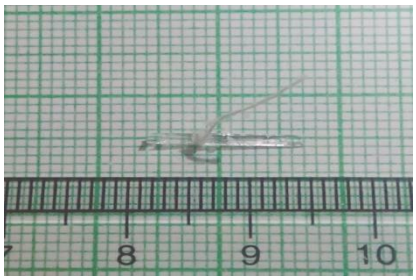


**Fig1b**

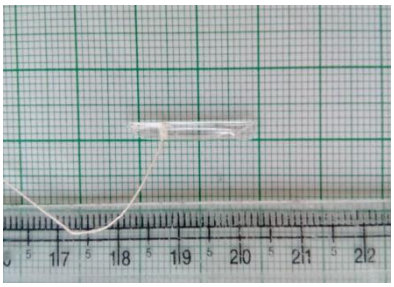


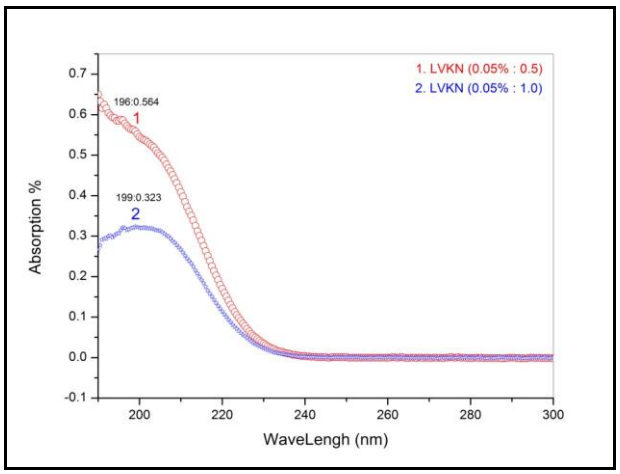
**Fig1c**

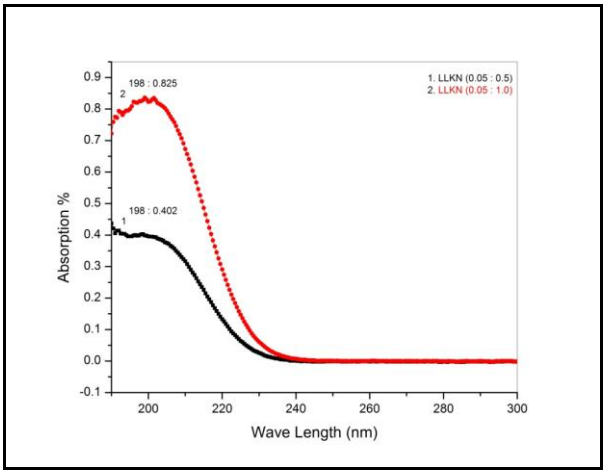
**Signle Crystal; Fig.1c.LPKN Single Crystal**

## 3.0. Result and discussion

### *3.1. UV-Visible spectrum*

Optical studies for grown solid LVKN, LLKN and LPKN crystals of mentioned molecular ratios were carried out through Shimadzu UV 1700 spectrometer in the range of 150 -1100 nmshown in fig-2.



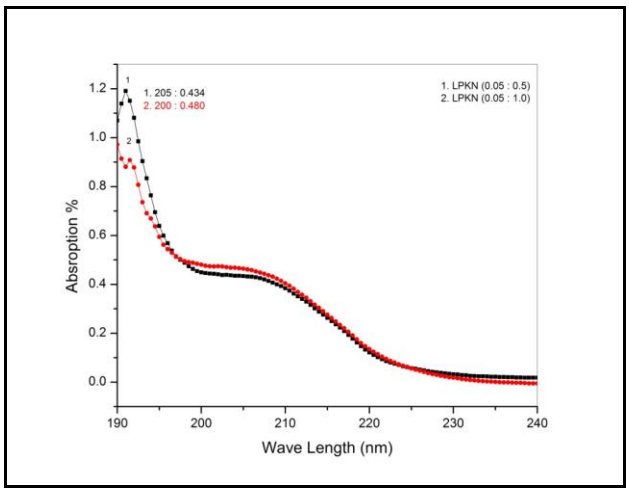



**Fig .2a,2b,2c: UV-Visible spectrum**

The optical absorption with lower cut off wavelength below 205 nm for all titled crystals, shown in table 1 respectively makes this crystals suitable for UV tunable laser and Second harmonic device application (3-6 )

**Table 1: UV-Visible Spectrum for LVKN, LLKN and LPKN crystals**

| **Crystal** | **L-Valine+$KNO_3$** | | **L-Leucine+$KNO_3$** | | **L-Phenylalanine+$KNO_3$** | |
|---|---|---|---|---|---|---|
| Molecular ratio | 0.05:0.5 | 0.05:1.0 | 0.05:0.5 | 0.05:1.0 | 0.05:0.5 | 0.05:1.0 |
| Absorption% | 0.564 | 0.323 | 0.402 | 0.825 | 0.434 | 0.480 |
| Wavelength(nm) | 196 | 199 | 198 | 198 | 205 | 200 |

### 3.2. Tauc's Plot:

The energy band gaps of LVKN, LLKN, and LPKN of the same molar ratios were carried out by using Tauc's plot( 7-8) as shown in fig(3). The indirect optical energy gap were identified for titled crystals are noted in table 2.

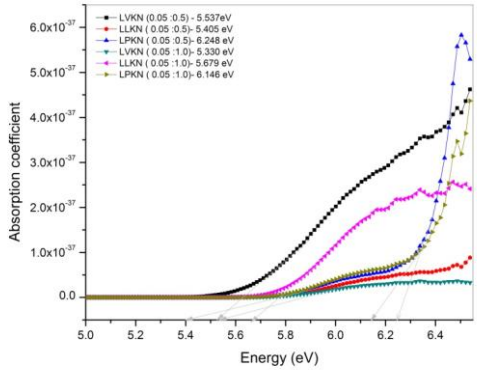



**Table 2 Tauc's Plot for LVKN,LLKN and LPKN crystals**

| **Crystal** | **L-Valine+$KNO_3$** | | **L-Leucine+$KNO_3$** | | **L-Phenylalanine+$KNO_3$** | |
|---|---|---|---|---|---|---|
| Molecular ratio | 0.05:0.5 | 0.05:1.0 | 0.05:0.5 | 0.05:1.0 | 0.05:0.5 | 0.05:1.0 |
| Optical Energy gap | 5.537 | 5.33 | 5.405 | 5.679 | 6.248 | 6.146 |

### 3.3. FT-IR Spectral analysis

The FT-IR spectra of the grown LVKN, LLKN, and LPKN single crystal were recorded in the field range of 500-4000cm-1as shown in Fig 4. The respective absorption frequencies with their assignments are listed in the table 3. The Carboxyl functional group COO- and COOH of LVKN were found at 1583, 1396 cm-1 and amine groups NH2+were found at 1502 cm-1. The inorganic alkali metal functional group N-O and HO-P-OH influences were found at 821 cm-1 and 748 cm-1. Similarly the same functional group of LLKN single crystal were found at 1562cm-1, 1383 cm-1, 1494 cm-1, 825 cm-1 , and 746 cm-1. A small functional group were shifted and founded at the same region for LPKN crystals and all the crystal assignments were in good agreements to the reported values (9-15)

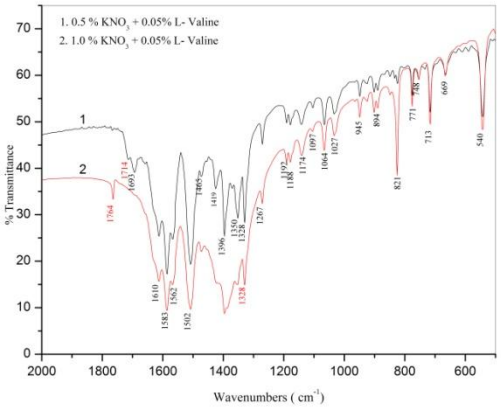



Fig.4a1 600-2000cm-1

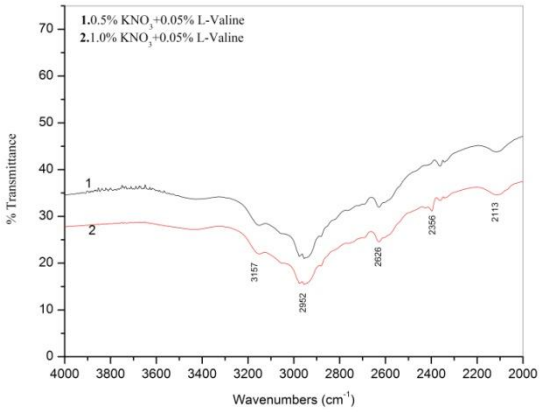



Fig.4a2 2000-4000cm-1

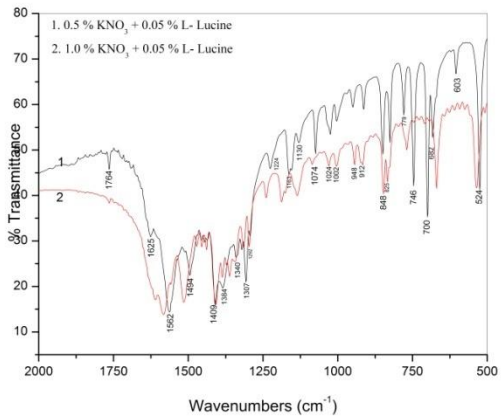



Fig.4b1. 600-2000cm-1

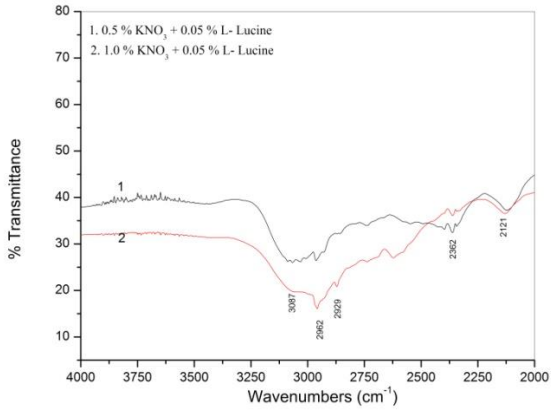



Fig.4b2. 600-2000cm-1

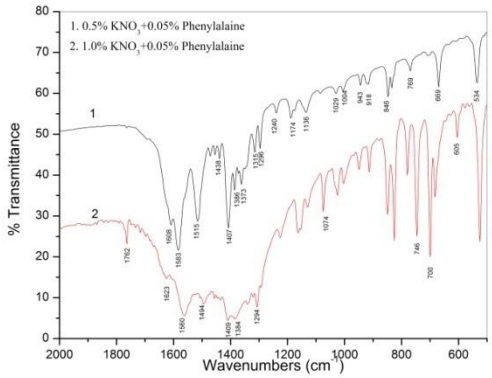



Fig.4c1 600-2000cm-1

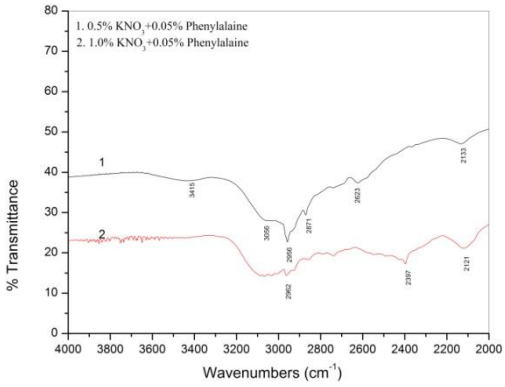
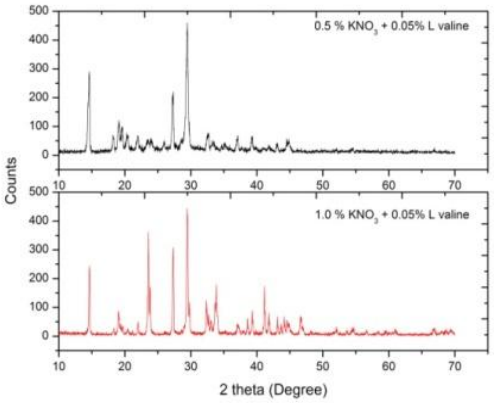
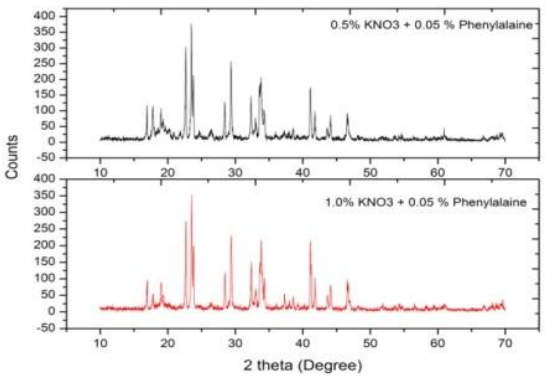


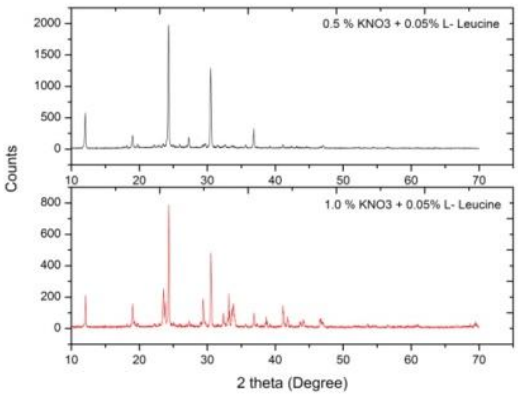

Fig.4c2 600-2000cm-1

### 3.4. Powder X-ray diffraction (XRD) analysis

The grown crystals were characterized by Powder XRD technique to confirm the crystallinity. The powder samples were scanned in the range between 10°-70° at a scan rate of 2°/min is shown in the fig-5. The evaluated cell parameters of all grown crystals are listed in the table 4 which are in good agreement with the reported works (16-20). The obtained peaks and evaluated lattice parameters revealed that the addition of $KNO_3$ did change the shape of the structure of mentioned crystals.




**X-ray diffraction graph of titiled crystal**

**Table 3: Functional frequencies of vibrations of LVKN, LLKN and LPKN crystals**

| L-Valine+$KNO_3$ | | L-Leucine+$KNO_3$ | | L-Phenylalanine+$KNO_3$ | | Assignment |
|---|---|---|---|---|---|---|
| 0.05:0.5 (mole ratio) | 0.05:1.0 (mole ratio) | 0.05:0.5 (mole ratio) | 0.05:1.0 (mole ratio) | 0.05:0.5 (mole ratio) | 0.05:1.0 (mole ratio) | |
| 3157 | 3157 | 3087 | 3087 | - | - | N-H, Stretching, Asymmetric $NH^{3+}$ Vibration |
| 2952 | 2952 | 2962 | 2962 | 2962 | 2962 | Asymmetric Stretching $CH_2$ vibration |
| - | - | - | 2929 | 2871 | - | Asymmetric Stretching $CH_2$ vibration |
| 2626 | 2626 | 2362 | 2362 | - | 2397 | N-H stretching, Combination of $NH_3^+$ bonding |
| 2356 | 2356 | 2121 | 2362 | 2133 | 2121 | |
| - | 1764 | 1764(s) | 1764 (w) | - | 1762 | C=O stretching vibration[(a)] |
| 1693 | 1610 | 1625(w) | 1625(w) | 1608 | 1623 | Asymmetric bending of $NH_3^+$ |
| 1583 | 1583 | 1562 | 1570 | 1583 | 1560 | $NH_3^+$ symmetric bending, Asymmetric stretching of $COO^-$ |
| 1502 | 1500 | 1494 | 1502 | 1515 | 1494 | $NH_2^+$ Asymmetric bending, symmetric deformation of $NH_3^+$ |
| 1465 | 1465 | 1438 | 1438 | 1438 | 1438 | $CH_3^+$ Asymmetric stretching, Symmetric $CH_3$ vibration |
| 1419 | - | 1442 | 1442 | 1442 | 1442 | |
| 1396 | 1388 | 1409 | 1409 | 1407 | 1409 | $CH_2$ symmetric bending, $COO^-$ group symmetric vibration |
| - | - | 1384 | 1384 | 1386 | 1384 | $CH_3$ deformation |
| 1350 | 1350 | 1340 | 1340 | 1315 | - | $CH_2$ Wagging motion |
| 1328 | 1328 | 1307 | 1307 | 1296 | 1294 | $CH_2$ wagging, Symmetric bending $CH_3$ |
| 1267 | 1267 | 1163 | 1183 | 1174 | 1174 | $CH_3$ Rocking, $NH_3^+$ rocking vibration |
| 821 | 824 | 848 | 848 | 846 | 846 | COO rocking, N-O stretching |
| 748 | 771 | 746 | - | 769 | 746 | N-O stretching |
| 713 | 713 | 700 | - | 699 | 700 | COO- bending |
| 669 | 662 | 682 | 660 | 669 | 672 | COO- bending |
| - | - | 603 | - | - | 605 | Presents of substitute ring 1,4 distributions |
| 540 | 540 | 524 | 524 | 534 | 526 | COO- Rocking, K-O stretching |

**Table 4: Comparison cell parameters of LVKN, LLKN and LPKN crystals**

| **Crystal** | **L-Valine+$KNO_3$ (LVKN)** | | | **L-Leucine+$KNO_3$ (LLKN)** | | | **L-Phenylalanine+$KNO_3$ (LPKN)** | | |
|---|---|---|---|---|---|---|---|---|---|
| Molecular ratio | Reported value | Present value | | Reported value | Present value | | Reported value | Present value | |
| | | 0.05:0.5 | 0.05:1.0 | | 0.05:0.5 | 0.05:1.0 | | 0.05:0.5 | 0.05:1.0 |
| Crystal system | Mono clinic[18] | Mono clinic | Mono clinic | Mono clinic[19] | Mono clinic | Mono clinic | Mono clinic[22] | Mono clinic | Monoclinic |
| Lattice parameters **α** | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 |
| **β** | 90.66 | 107.18 | 102.34 | 94.06 | 113.43 | 95.14 | 101.19 | 90.88 | 103.44 |
| **γ** | 90.0 | 90.0 | 90.0 | 90.0 | 90 | 90 | 90.0 | 90.0 | 90.0 |
| **a** | 9.701 | 9.815 | 9.756 | 14.666 | 14.876 | 14.882 | 11.06 | 10.43 | 11.20 |
| **b** | 5.261 | 6.154 | 5.879 | 5.324 | 5.322 | 5.342 | 5.34 | 5.22 | 5.43 |
| **c** | 11.953 | 12.43 | 12.184 | 9.606 | 9.652 | 9.642 | 11.48 | 10.86 | 11.62 |
| Volume | **610.04** | **692.50** | **614.04** | **748.00** | **754.13** | **752.63** | **667.00** | **658.40** | **669.32** |

**Table 5: Comparisons of SHG signal outputs and efficiencies**

| **Crystal** | **L-Valine+$KNO_3$** | | **L-Leucine+$KNO_3$** | | **L-Phenylalanine+$KNO_3$** | |
|---|---|---|---|---|---|---|
| Molecular ratio | 0.05:0.5 | 0.05:1.0 | 0.05:0.5 | 0.05:1.0 | 0.05:0.5 | 0.05:1.0 |
| **KDP reference Output voltage** | **55mV** | **55mV** | **32mV** | **32mV** | **38mV** | **38mV** |
| Crystals output voltage | 44mV | 37mV | 16.7mv | 17.1mv | 128mV | 134mV |
| Efficiency % | 1.25 | 1.48 | 1.91 | 1.87 | 0.29 | 0.28 |

### 3.5. SHG studies

Kurtz (20) second Harmonic Generation (SHG) test were carried out for titled crystals to find NLO nature of the material (21). The crystalline powdered sample was packed in a capillary tube laser of pulse with 8 ns a wave length of 1064nm and 10 Hz fundamental radiation. The efficacy of SHG was compared with KDP material in table (5)

## 4.0. Conclusion

The single crystals of LVKN, LLKN and LPKN were grown by slow evaporation technique. FT-IR study shows the functional group identity. The crystalline nature and structures of mentioned crystals were confirm by X-ray diffraction analysis. The good optical suitability was confirmed through UV-Vis Spectrum. The encouraging crystal growth characteristics and their properties of titled crystals recommend it as a potential material for SHG device application. To have a better understanding of the newly formed material it is also essential to study the molecular interaction of the chosen samples by exposing it to ultrasonic frequency.

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