



## Growth and Characterization of Urea L-Valine An Organic non Linear Optical Crystal

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### ABSTRACT

Single crystals of new organic nonlinear optical material urea L-valine were grown by slow evaporation solution growth technique at room temperature. Elemental composition percentages were analysed using CHN study. Crystalline nature of the sample was confirmed by powder XRD. A functional group present in the crystal was identified using FT-IR spectral analysis. An optical transmittance study was also carried out for the crystal. Dielectric studies were performed with respect to temperature at various frequencies (50Hz-5MHz). Photoconductivity study reveals the negative photoconductivity nature of the crystal. Powder second generation efficiency of the crystal was studied using modified kurtz and perry technique.

**Key words:** Nonlinear, Powder X-ray diffraction, Optical, Dielectric, Photoconductivity, Single crystal XRD.

### INTRODUCTION

The search for new organic nonlinear optical crystals has been of great interest because of their wide range of potential applications such as frequency doubling, optical switching, optical disk data storage, optical modulation, laser remote sensing and medical diagnostics. These materials attracting significant attention as they possess large nonlinear optical susceptibilities, ultrafast nonlinear response time, high laser damage threshold and scope for introducing desirable characteristics by multifunctional substitutions<sup>1-3</sup>. For NLO device applications still there is a demand for good quality crystals with higher efficiency. For the past ten

years amino acids are playing a vital role in the nonlinear optical crystal growth. They individually exhibit nonlinear properties as they possess proton donor carboxyl acid (COO<sup>-</sup>) and proton acceptor amino (NH<sub>3</sub><sup>+</sup>) group also in solid state they exist as zwitterions. Amino acid crystals play a major role in NLO applications such as L-valine, L-alanine, L-proline, L-leucine, L-histidine, L-arginine and L-phenylalanine. Worldwide urea and its derivatives are extensively used in crystal engineering and supramolecular chemistry for their flexibility in the synthesis of functional materials. Also for a long time it is used as a model system for crystals from solution growth and reference material in Powder SHG<sup>3-9</sup>.

In the present work urea and L-valine single crystals were grown by slow evaporation solution growth technique. The grown crystal was characterized by various characterization techniques such as CHN analysis, powder XRD, FT-IR, optical transmittance, dielectric, photoconductivity and powder SHG measurements.

## MATERIALS AND METHODS

### Crystal growth

Urea L-valine single crystals were grown by slow evaporation solution growth technique at room temperature. Urea and L-valine were separately taken in equimolar ratio and dissolved in double distilled water and stirred separately for half an hour. Then the solutions were mixed together and stirred well for about 5 hrs. the saturated solution was filtered using whatman (No:42 grade) filter paper. The filtered solution was kept at undisturbed place for crystal growth. After two weeks optically good quality single crystals were obtained from the mother solution. Fig. 1 shows the quality of the crystal.

## RESULT AND DISCUSSION

### CHN analysis

The elemental composition percentage of urea L-valine crystals were analysed using Vario EL III Elemental analyser. The experimental C, H and N percentages were compared with theoretical values and listed in Table 1. Which confirms the presence of the compound.

### Powder XRD

Powder X-ray diffraction studies for the grown crystals were carried out using RICH SIEFERT X-ray powder diffractometer using  $\text{CuK}\alpha$  ( $\lambda=1.5405 \text{ \AA}$ ) radiation. Sample was scanned over  $2\theta$  the range of 5-80 at rate of  $3^\circ/\text{min}$ . The crystals were finely grained into powder in uniform size and subjected to analysis. Crystalline nature was quite clear from the occurrence of sharp peaks at specific Bragg's angles. Fig. 2 shows the recorded spectrum. The powder XRD result of this crystal was compared with previous reports in which urea and L-valine were mixed with acids and metals. From the XRD peak intensity it is concluded that in the present work crystalline nature was very high while comparing previous reports<sup>10-15</sup>.

### FT-IR analysis

The middle IR spectrum of urea L-valine crystal is carried out at room temperature in the spectral range of  $4000-400\text{cm}^{-1}$  by KBr pellet technique. The recorded spectrum is shown in Fig. 3. The band observed at  $3344$  and  $3444 \text{ cm}^{-1}$  are assigned to OH and  $\text{NH}_2$  symmetric and asymmetric stretching vibrations. The torsional mode of  $\text{NH}_3$  is observed at  $543 \text{ cm}^{-1}$ . The peak at  $669 \text{ cm}^{-1}$  is due to OH bending vibration. The symmetric and asymmetric stretching vibrations of  $\text{CH}_2$  are observed at  $2881$  and  $2947 \text{ cm}^{-1}$ . Bands observed at  $1029$  and  $1469 \text{ cm}^{-1}$  are assigned to N-C-N symmetric and asymmetric stretching vibration of urea. Frequencies at  $1431$  and  $1327 \text{ cm}^{-1}$  are assigned to C-O stretching vibration of L-valine. The symmetric and asymmetric stretching of  $\text{COO}^-$  vibrations (carboxylate anion) are found at  $1585$  and  $1431 \text{ cm}^{-1}$  respectively. The absorption band at  $1068$  and  $1585 \text{ cm}^{-1}$  are assigned to CN and C=O stretching vibrations respectively.  $\text{CH}_2$  bending vibration is observed at  $1350 \text{ cm}^{-1}$ .  $\text{NH}_2$  in-plane bending vibration appears at  $1585 \text{ cm}^{-1}$ . The C-C skeletal vibration is observed at  $775 \text{ cm}^{-1}$ . The peak around  $1145 \text{ cm}^{-1}$  is due to  $\text{NH}_2$  rocking vibration.  $\text{COO}^-$  rocking vibration could be assigned to peaks  $543$  and  $428 \text{ cm}^{-1}$ . The frequencies at  $713$ ,  $821$  and  $948 \text{ cm}^{-1}$  are correspond to CH out-of-plane bending vibration.

### Optical studies

Optical transmittance is one of the important desirable properties for identifying the potential NLO material. Optical transmittance studies were carried out in the wavelength range between  $200-1100\text{nm}$  using a Perkin-Elmer lambda 35 spectrometer. Fig. 4 represents the transmittance spectrum of urea L-valine crystal. Crystal exhibits large transmittance in the visible region, possessing a transmittance greater than 80% for incident wavelength ranging from  $300$  to  $1200\text{nm}$ . Lower cut off wavelength of

**Table1: Elemental composition percentage of urea L-valine crystals**

Elements	Experimental(%)	Theoretical (%)
Carbon	40.78	40.67
Hydrogen	8.42	8.53
Nitrogen	23.6	23.71

the crystal is 245 nm. Optical band gap ( $E_g$ ) of the material was evaluated by the extrapolation of the linear part<sup>16-17</sup>. Which is represented in Fig. 5 from the graph band gap energy is calculated as 3.03eV. Large transmittance and high band gap is one of the important for materials possessing greater possibilities for nonlinear device applications<sup>18-20</sup>.

### Dielectric studies

Dielectric studies for the crystals were performed using Hioki 3532-50 LCR meter. Measurements were carried out in the frequency range from 50Hz to 5MHz at various temperature (303 to 378K). Dielectric constant of the crystals were calculated using the capacitance value by the given relation

Where C is the capacitance and d is the thickness of the sample, A is the cross sectional area of the sample and  $\epsilon_0$  is the free space permittivity of the sample. Fig. 6 shows dielectric constant with respect to log frequency. From the figure it is observed that dielectric constant is very high at low frequency and becomes low at high frequency (Upto 1MHz) and attains minimum value at higher frequencies (Above 1MHz). High dielectric constant at low frequency is due to the prescence of all four polarizations namely electronic, ionic, space charge and orientation. Low value at higher frequency is due to significant loss of these polarizations<sup>21</sup>. Fig. 7 shows the dielectric loss Vs log frequency. The dielectric loss is very low at high frequency it confirms that grown crystal possess less defects with enhanced optical quality. Materials

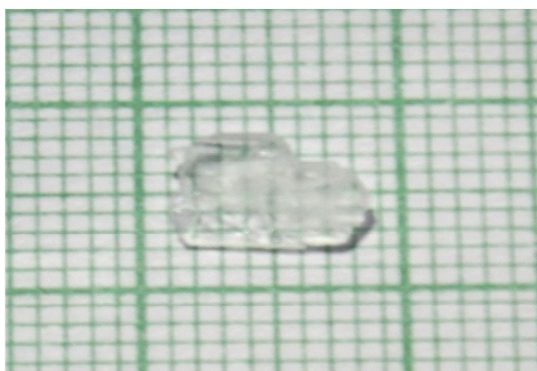


Fig. 1: Photograph of as grown crystal

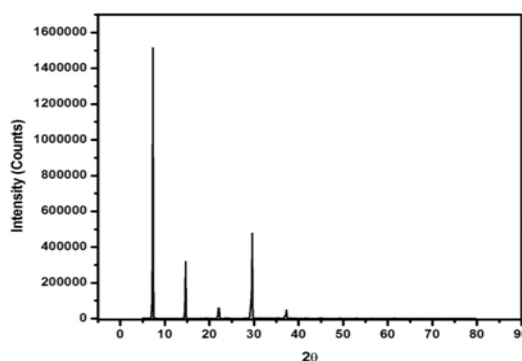


Fig. 2: Powder XRD spectrum

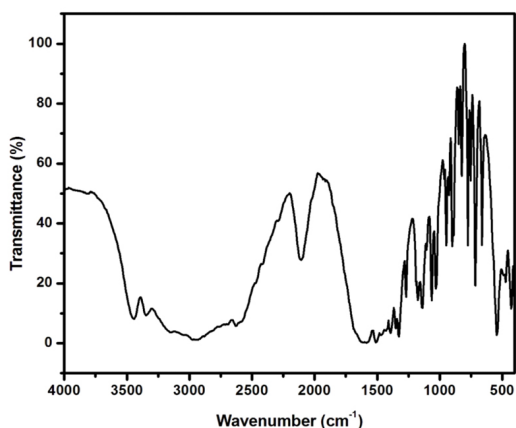


Fig. 3: FT-IR spectrum.

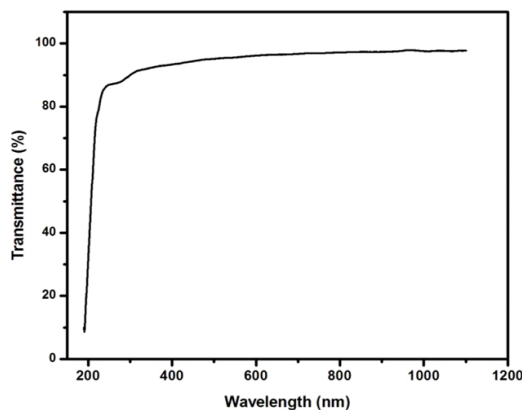


Fig. 4: Optical transmission spectrum

with high dielectric constant and low dielectric loss can be very much useful for capacitor and heating devices applications<sup>22</sup>.

### Photoconductivity

Photoconductivity studies were carried out at room temperature using Keithley 6512 electrometer. Crystal was silver pasted on opposite faces and thin copper wire was connected both sides on the sample and it is connected in series with electrometer. The sample was protected from all the radiation. The applied input voltage was increased from 10 to 100V and resultant dark current was recorded. Then the samples were exposed to radiation from 100W halogen lamp containing iodine vapour and tungston filament. Phtocurrent was recorded for the

same input voltage. Fig. 8 shows the photo current and dark current response for the sample. From the figure it is concluded that dark current is higher than photocurrent and this phenomena is called negative photoconductivity. It may be due to the reduction of charge carriers in the prescence of radiation. Further it was explained by Stockman model<sup>23</sup>. Negative photoconductivity materials can be used for UV and IR detector applications<sup>24</sup>.

### Powder SHG

Powder second harmonic generation efficiency of the grown crystal was determined using modified Kurtz and Perry method<sup>25</sup>. Q-switched mode locked Nd:YAG laser was used as a optical source. The crystals were grained into powder and densely

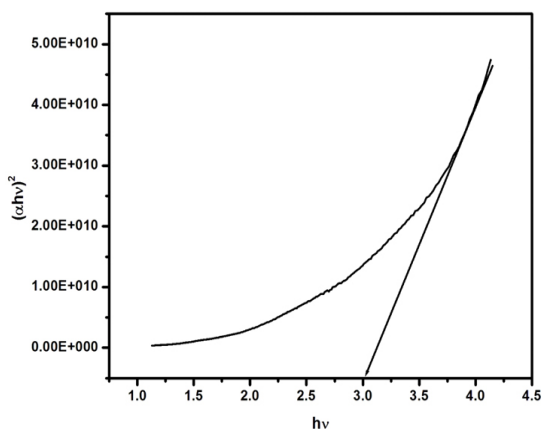


Fig. 5: Determination of optical band gap

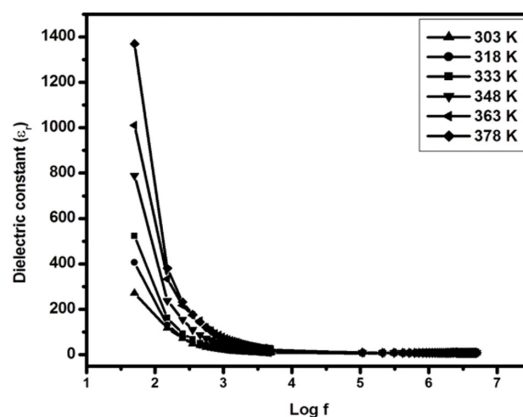


Fig. 6. Dielectric constant Vs Log f

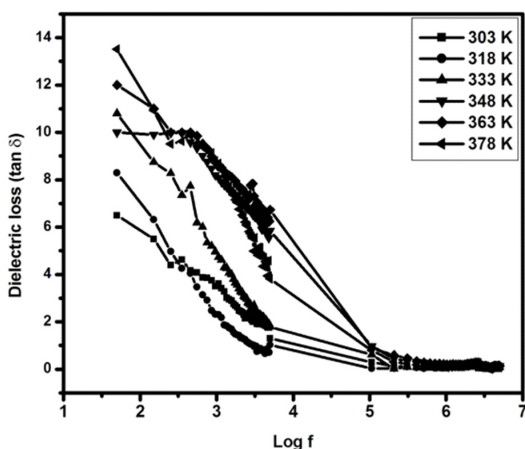


Fig. 7: Dielectric loss Vs Log f

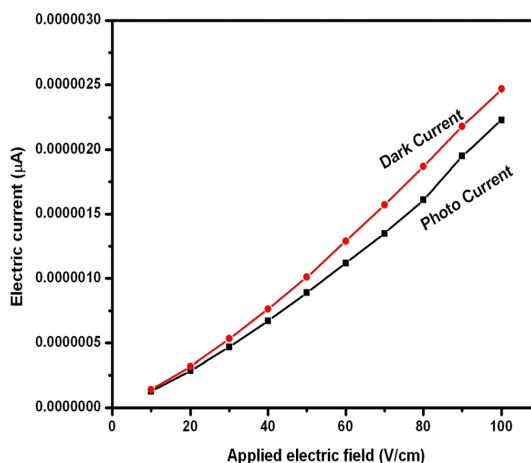


Fig. 8: Photoconductivity response for the

packed between two glass slides. The input energy was measured using power meter and it is 4.6mJ/s. Powdered KDP crystal was used as a reference material. The laser light (1064nm) was focussed on to the sample. The green output (532nm) was collected by a photomultiplier tube and finally measured on the storage oscilloscope (CRO) as output voltage. Output signal of 15mV is obtained for the titled compound while the KDP is 7.4mV. It is concluded that title compound is times 2.02 times greater than that of reference KDP.

#### Single crystal XRD analysis

The unit cell parameters are determined by using the singlecrystal X-ray diffraction data obtained with a four-circle Nonius CAD4/diffractometer (MoK $\alpha$ ,  $\lambda = 0.710738 \text{ \AA}$ ). The unit cell parameters are  $a = 5.771(1) \text{ \AA}$ ,  $b = 6.012(1) \text{ \AA}$ ,  $c = 12.295(5) \text{ \AA}$ ,  $\alpha = 90^\circ$   $\beta = 90^\circ$   $\gamma = 90^\circ$  and volume =  $426.8(2) \text{ \AA}^3$ . From the data, it is observed that the grown crystal is belongs to orthorhombic system.

#### CONCLUSION

Urea L-valine single crystals were grown by slow evaporation solution growth technique at room temperature. Crystalline nature of the compound was confirmed by powder XRD analysis. A functional group present in the crystal was identified using FT-IR studies. Optical transmission study confirms the quality of the crystals for NLO applications. Optical band was found to be 3.03eV. In dielectrics dielectric constant is very high at low frequency. Photoconductivity study reveals the negative photoconductivity nature of the crystal. powder SHG efficiency of the grown crystal is 2.02 times greater than KDP.

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