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Optical and Mechanical Studies of a Nonlinear Single Crystal: Urea Doped Dl-Alanine Oxalate

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***Abstract*--** Single crystals of urea doped dl-alanine oxalate have been grown by slow evaporation method at room temperature. The harvested crystals were characterized by various studies such as solubility, FTIR spectral analysis, UV-visible spectral studies, microhardness studies, etc. The properties and the results are presented and discussed. Fourier Transform Infrared spectroscopy is performed to study the possible molecular vibration of the crystal. The functional groups and vibrational frequencies were identified using spectral analysis. UV-Vis transmittance spectrum was recorded for the sample to analyze the transparency in visible region. From the graph cut-off frequency is obtained to calculate the band gap energy. The mechanical properties of the grown crystals were subjected to Vicker's hardness test. Yield strength and elastic stiffness constant were estimated.

***Keywords*--** *FTIR , UV-visible spectral studies, microhardness*

I. I INTRODUCTION

An amino acid consists of a central carbon atom attached to a carboxyl group (-COOH), an amino group ($-NH_2$), a hydrogen atom, and a side group (-R), giving the general formula R-CH-NH_2-COOH. Only the side group differs from one amino acid to another. Essential amino acids are those that an organism must obtain readymade from its environment. Amino acids are the building blocks used to make proteins and peptides. The different amino acids have interesting properties because they have a variety of structural parts which result in different polarities and solubilities.

The key elements of an amino acid are carbon, hydrogen, oxygen and nitrogen. Amino acids are important in nutrition and are commonly used in food technology, industry and biochemistry. In industry, applications include the production of biodegradable plastics, drugs and chiral catalysts.

DL-alanine is one among the rare amino acid racemates crystallizing in a non-centrosymmetric space group.

II. SYNTHESIS OF UREA DOPED DL-ALANINE

Here DL-alanine is mixed with oxalic acid, an organic acid, and urea to form urea doped DL-alanine oxalate. To synthesize this salt, DL-alanine and oxalic acid were taken in 1:1 molar ratio, 1% urea is doped with it and dissolved in de-ionized water. The solution was stirred well using hot plate magnetic stirrer at 60°C. The salt of urea doped DL-alanine oxalate was obtained till the solution evaporated out completely.

III. SOLUBILITY STUDIES

The DAOU sample was finely powered for solubility study. A known amount of a solvent was taken in a beaker. At room temperature, the DAOU was added until the dissolution stopped. The solubility was determined by gravimetrical method. The same procedure was repeated by increasing the temperature (ie. 40^0C, 50^0C, 60^0C). DAOU was sparingly soluble in organic solvents like acetone, ethanol & methanol. Water was found to be a better solvent for growing single crystals of DAOU because of high solubility of DAOU sample in water when compared to the other organic solvents.

The variation of solubility of DAOU with temperature in deionized water is shown in fig.1. From the solubility graph it is noticed that the solubility increases with temperature and sample has positive temperature coefficient to solubility .The positive slope of the solubility curve enables the growth of DAOU crystal by slow evaporation method at room temperature.

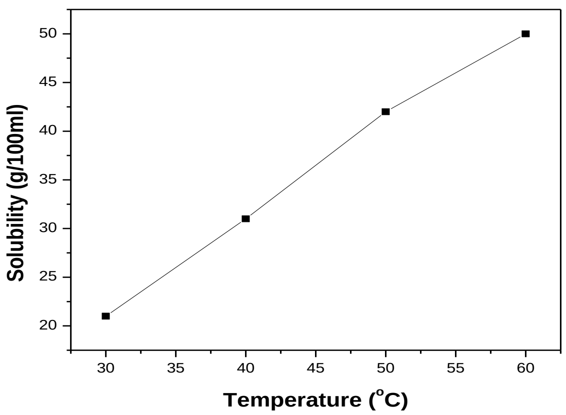

Figure 1: Solubility curve of DAOU sample

IV. EXPERIMENTAL PROCEDURE

The single crystals of urea-doped DL- alanine were grown by solution method with slow evaporation technique. Using the solubility data, the saturated solution was prepared at 30°C and stirred well for about 2 hours. Then the solution was filtered and it was taken in a beaker for crystallization. The beaker was covered with perforated polythene papers and they were kept in a vibration free platform at room temperature (30°C). Over a period of 10-15 days, The solvent gradually evaporates leading to supersaturation. The excess of the solute was deposited at the bottom and big-sized crystals were harvested. The size of the crystal was 18 mmx17mm x 6mm

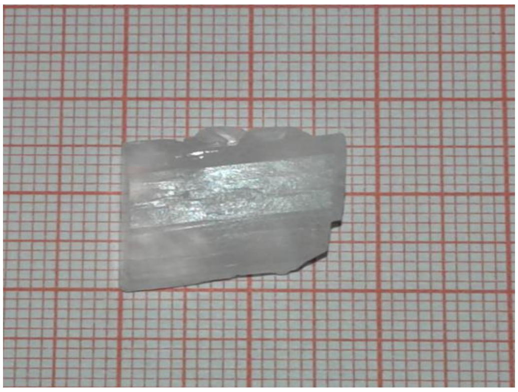

Figure 2: Single crystal of DAOU sample

V. FOURIER TRANSFORM INFRARED SPECTRAL STUDIES (FTIR)

FTIR Studies are important in the investigation of molecular structure of crystals. This study involves examination of stretching, bending and twisting vibrational modes of atoms in a molecule and hence it helps to identify the functional groups of samples. The infrared spectrum of DAOU has been recorded in the range of 400-4500cm^{-1}. KBr pellet technique was used to take FTIR spectra of DAOU crystals are presented in the figure.

The peak at 1413cm^{-1} corresponding to COO$^-$ stretching of the amino acid. 1621cm^{-1} C=N stretching mode occurs. The absorption band at 1646cm^{-1} confirms the presence of N-H Bending. The peak at 1743cm^{-1} corresponding to C=O stretching vibration. The broad bands around 3034cm^{-1} corresponding to NH stretching vibration. The peak at 3447cm^{-1} O-H stretching vibration. The complete absorption bands and their assignments for the grown DAOU sample are pro- vided in the **Table 1**.

Table 1 FTIR spectral assignments of DAOU sample

Frequency Range	*Band Assignments*
422	NH_3^+ torsion
497	COO^- rocking
556	NH_3^+ torsion
597	COO^- wagging
678	COO^- bending
1112	NH3 + rocking
1241	OH bending
1413	COO^- Stretching
1473	NH_3^+ deformation
1622	C=N Stretching
1646	N-H Bending
1743	C=O Stretching
3034	N-H Stretching
3408	NH_3^+ asymmetric and OH stretching
3447	O-H Stretching

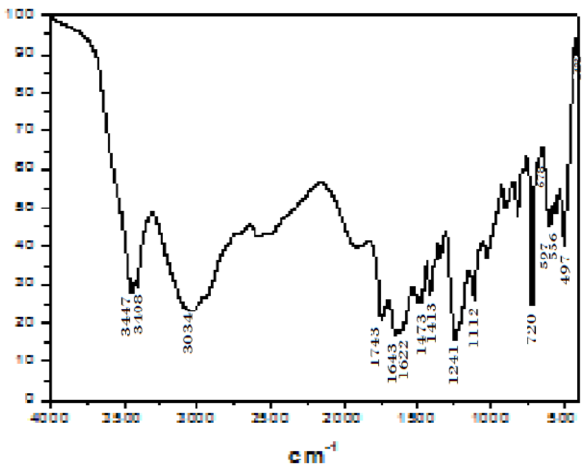

Figure 3: FTIR spectrum of DAOU sample

VI. UV-VISIBLE SPECTRAL STUDIES

The UV-visible spectral analysis was made between 190nm and 1100nm, which covers near ultraviolet (200nm-400nm), visible (400-800nm) and far- infrared (800-1200nm) regions. The UV-visible transmittance and absorption spectra of DAOU samples are shown in the figure 4.

Transparency is high in visible region. No absorption is observed in the entire UV and visible region. In the case of DAOU, at 222 nm a fall of transmittance was observed indicating a single transition in the near UV region. The cut-off wavelength of the grown DAOU crystal is found to be 222 nm from UV-visible-NIR spectral studies. The lower cut off absorption is an encouraging optical property seen in doped DAOU crystals and is of vital importance for NLO materials.

The Band gap of DAOU is determined using the relation, $E_g = hc/\lambda$ where h is Planck's constant, c is the velocity of light and λ is the wavelength of light and the value obtained is 5.59 eV. The large value of energy gap DAOU crystal indicates that it is an insulating material. As the DAOU crystal had good transmission in the entire visible and near IR region and hence it is a suitable candidate for optical applications.

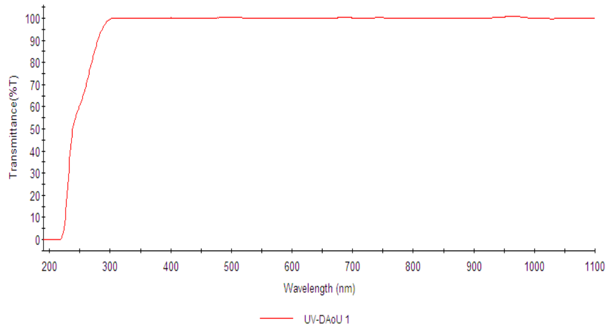

Figure 4. UV-Visible spectrum of DAOU

VII. MICRO HARDNESS STUDIES

The selected smooth surface of DAOU was used for micro hardness measurements at room temperatures, using a Vickers's micro hardness tester attached to an incident-light microscope (Leitz-Wetzler microscope). Keeping the indenter at right angles to the crystal plane for 10 s in all cases. An average of 10 diagonal length of the indentation mark was measured using an optical micrometer eyepiece at a magnification of 500:1.

The hardness number was calculated using the relation

$H_v = 1.8544\ P/d^2\ \text{kg}/\text{mm}^2$

where P is the applied load in kg and d is the diagonal length of the indentation impression in millimeter. The plot between hardness number (H**v**) and load (P) for doped DAOU crystal is shown in Figure 5.

The variations of Vickers hardness number (H_v) with the applied load for the samples are shown in figures 5. The increase of micro hardness with increasing load is in agreement with the indentation size effect (ISE).

A Plot obtained between log p against log d gives a straight line which is derived from the Meyer's law, the relation connecting the applied load is given by $p = ad^n$. Hence, n is the Meyer's index or work hardening coefficient that has been calculated from the slope of the straight line from the figure 6. The value of n for DAOU is found to be 3.857. According to Onitsch, if n is greater than 1.6 the material belongs to the category of soft materials. Therefore the crystal DAOU is soft material. It decomposes at high temperature and fairly soluble in water

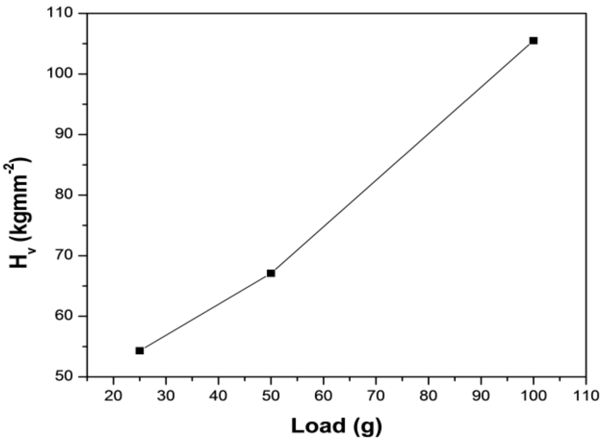

Figure 5: Variation of Vickers micro hardness number (H_v) with the applied load for DAOU

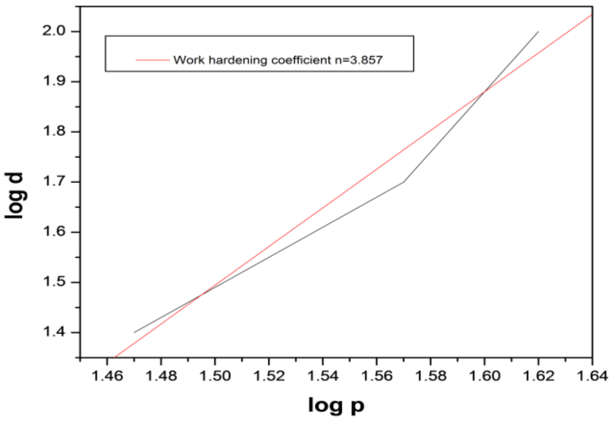

Figure 6: Variation of log p with log d for DAOU crystal

CONCLUSION

DAOU crystals have been grown by slow evaporation technique at room temperature. The grown crystals are found to be transparent and colourless with well defined external appearance. Good quality single crystal of DAOU is of size 18 x 17 x 6 mm^3 has been grown.

From the Solubility graph we found that solubility increases with temperature. From UV-visible spectra, The crystal has good transmission in the entire visible and NIR region. It is found that the cut off wavelength is found to be 222 nm. The band gap of DAOU determined using the relation hc/λ and the value obtained is to be 5.59 eV .

Vickers microhardness test reveals the fact that if the load is increased there is an increase in the hardness. Micro hardness analysis gives the hardness of the material n=3.857. the crystal belong to soft category material.

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