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Growth and Characterization of BIS Beta Alanine Urea Organic Single Crystal

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Abstract-- The title compound, Bis β-alanine urea (BBAU) was synthesized from aqueous solutions of β-alanine and urea taken in 2:1 molar ratio. The crystal reached a maximum size of 23 mm x 18 mm x 6 mm in a period of 15 days. It is observed that the grown crystal is well formed with sharp edges. Single crystals of β-alanine have been subjected to X-ray diffraction analysis to determine the crystal structure. The single crystal XRD data of BBAU shows that the cell constants a=6.124(3) Å, b=9.959(5) Å, c=13.967 (8) Å and α=90°, β=90 °, γ=90° and volume of the unit cell is 851.83 (2) Å^3. It belongs to orthorhombic crystal system. Fourier Transform Infrared spectral measurements have been carried out on the grown crystals in order to identify the functional groups. Optical transparency of the grown crystals was investigated by UV–Vis–NIR spectrum. The lower optical cutoff wavelength for this crystal was observed at 235 nm. The band gap value is calculated from the cut-off wavelength and is found to be 5.27 eV.

Mechanical hardness studies reveal that Vickers hardness number steeply increases as the load increases for the crystal. The dielectric constant and dielectric loss decrease with frequency and increase with temperature. The activation energies were calculated for the crystal.

I. INTRODUCTION

Amino acids and their complexes are the important organic or semi-organic materials used in the processing of optical devices. Researchers are always in search of new materials and their single crystal growth. From the stand-point of the search of new materials, amino acids offer a rich choice. Amino acids are bifunctional organic molecules that contain a carboxyl group as well as an amino group. In the solid state, amino acids contain a protonated amino group and de-protonated carboxylic acid group β-alanine is an amino acid in which the amino group is at the β- position from the carboxylate group. The grown crystals of bis β-alanine urea (BBAU) was characterized by various studies and the results are discussed.

II. SOLUBILITY AND GROWTH OF BBAU CRYSTAL

Bis β-alanine urea (BBAU) was synthesized from aqueous solutions of β-alanine and urea taken in 2:1 molar ratio. The evaporation of the solution yielded at 50 ^{o}C BBAU sample. The solubility study for the BBAU sample was carried out by gravimetrical method at different temperatures from 30 to 55 ^{o}C. The solubility curve for BBAU sample is given in figure 1. To grow single crystals of BBAU, slow evaporation method was employed. The saturated solution of BBAU in double distilled water was prepared at room temperature using the solubility data. The solution was mixed thoroughly in order to obtain homogeneous solution mixture. The solution was filtered and kept undisturbed in a dust-free environment. Tiny crystals were observed in the experimental vessel after the time period of 10 days. Macroscopic defect free transparent crystals were selected as seed for growing large sized single crystals of BBAU. The seed crystal was introduced into the mother solution. The crystal reached a maximum size of 23 mm x 18 mm x 6 mm in a period of 15 days. The as-grown crystals of BBAU are shown in Fig.2. It is observed that the grown crystal is well formed with sharp edges.

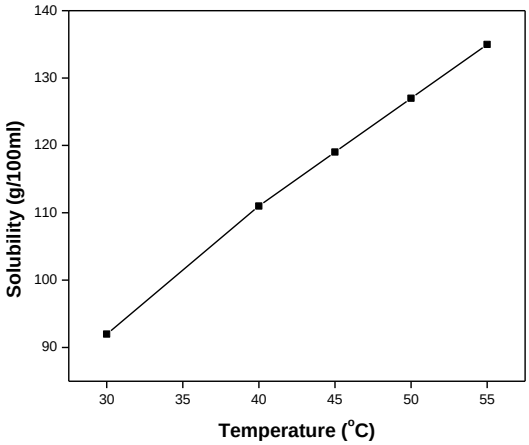

Figure 1: Solubility curve of BBAU crystal

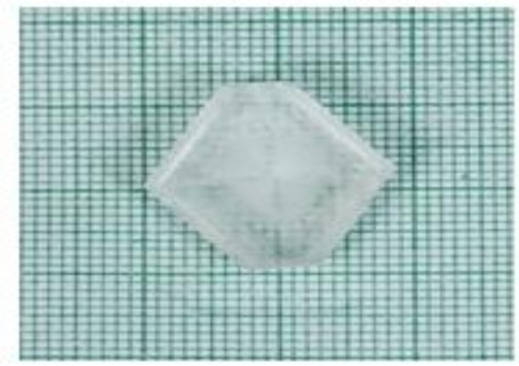

Figure 2: The harvested BBAU crystal

III. CHARACTERIZATION OF BBAU CRYSTAL GROWN BY SOLUTION METHOD

A. Single crystal XRD data

Single crystal XRD study was performed for the grown BBAU crystal to find the crystal structure. The cell parameters obtained by single crystal XRD study are: a=6.124 (3) Å, b=9.959(5) Å, c=13.967 (8) Å and α=90°, β=90 °, γ=90° and volume of the unit cell is 851.83 (2) Å^3. The BBAU crystal belongs to orthorhombic crystal system.

B. Identification of functional groups by FTIR spectral studies

The FTIR spectrum of BBAU crystal is shown in Fig. 3. In the sample BBAU, the NH_3^+ acts as a donor for hydrogen bond formation, whereas the oxygen atom of carbonyl group acts as an acceptor. In the FTIR spectrum of BBAU crystal, the broad and intense peak is due to NH_3^+ stretching and CH_2 asymmetric stretching appeared as strong absorption band in the range 2500–3500 cm^{-1}. The NO_2 scissoring is revealed by the peak at 530 cm^{-1}. The frequencies assigned for C-C stretching are around 836 and 1145 cm^{-1}. The peak at 1061 cm^{-1} is due to CN stretching. C–H in plane bending vibrations are observed at 1279 cm^{-1}. An intense sharp peak at 1410 cm^{-1} is due to the COO^- symmetric stretching. The frequency assigned for NH bending is at 1506 cm^{-1}, which shows the presence of urea part of the molecule. The sharp absorption bands at 1573 cm^{-1} and 1643 cm^{-1} correspond to the NH_3^+ asymmetric bending and carbonyl C=O stretching vibrations respectively. The absorption band at 1643 cm^{-1} confirms the presence of urea. The absorption at 2946 cm^{-1} is due to CH_2 asymmetric stretching & CH stretching. The assignments for the absorption peaks/bands are provided in the table 1..

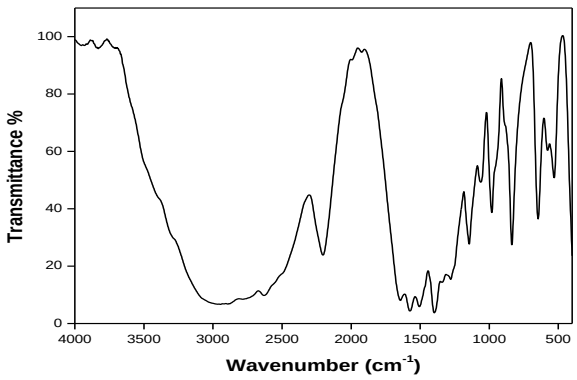

Figure 3: FTIR spectrum of BBAU crystal

Table 1: Observed IR band assignments for BBAU crystal

Wave number (cm^{-1})	Band assignments
530	NO_2 scissoring
836	C-C stretching
1061	CN stretching
1145	C-C stretching
1279	C–H in plane bending
1410	COO^- symmetric stretching
1506	NH bending
1573	NH_3^+ asymmetric bending
1643	Carbonyl (C=O) stretching & N-H bending(confirms the presence of urea)
2946	CH_2 asymmetric stretching & CH stretching

C. Optical studies

The transmittance and absorption optical spectra for BBAU sample between 190 and 1100 nm using spectrophotometer are displayed in the figures 4 and 5. The transmittance is found to be more in the entire visible and infrared regions. But around 235 nm there is a sharp decrease in transmittance due to absorbance leading to electronic excitation in this region. It is evident that the BBAU crystal has lower optical cut-off at 235 nm and it can be used in optical devices. The band gap value is calculated from the cut-off wavelength and is found to be 5.27 eV. The dielectric behaviour of the crystal depends on the band gap. As the crystal is colourless, there is very low absorbance in the entire visible region and shows maximum absorption at UV region. This is one of the most desirable properties of the crystals for the device fabrication.

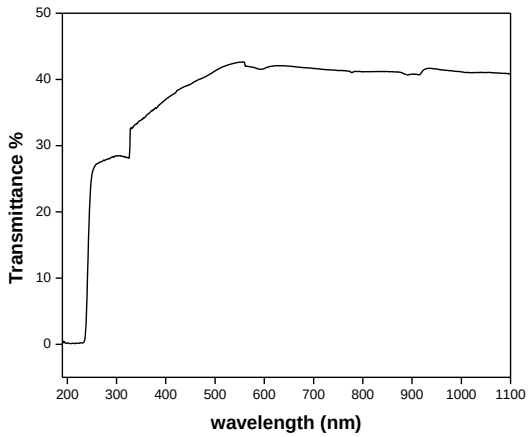

Figure 4: The UV-vis-NIR spectrum of BBAU crystal

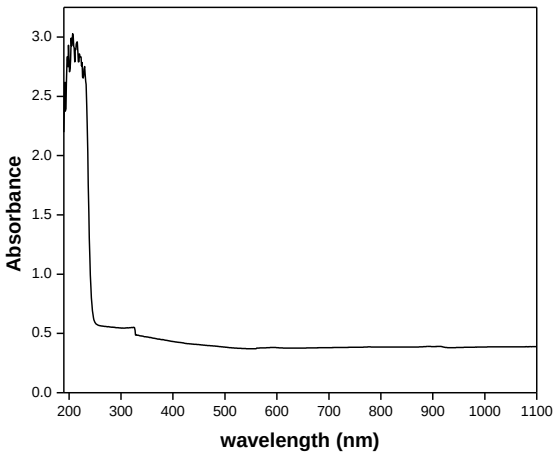

Figure 5: UV-visible absorbance spectrum of BBAU crystal

D. Mechanical Characterization

Micro hardness studies of any system have a direct correlation with the crystal structure and are very sensitive to the presence of any other phase or phase transition and lattice perfections prevalent in the system. The hardness of the material depends on the different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. The hardness test for BBAU crystal was carried out by Leitz micro hardness tester with a diamond pyramidal indenter. The diagonal length of the indentation for various applied loads is measured for a constant indentation period of 10 seconds. The Vickers hardness number (H_v) is calculated using the relation $H_v = 1.8544P/ d^2$ kg/mm^2 where P is the applied load in kg and d is the diagonal length in m. The variation of H_v with the applied load is shown in Fig. 6. It is observed that the microhardness value increases steeply with increase in applied

load. This can be explained qualitatively on the basis of depth of penetration of the indenter. For small loads, only a few surface layers are penetrated by the indenter and the measured hardness is the characteristics of these layers. With increase in load the over all effect is due to surface and inner layer of the samples. A plot of log P versus log d for the grown BBAU crystal is shown in fig.7. The work hardening coefficient is calculated to be 6.08. Since workhardening coefficient is more than 1.6, it belongs to a soft material.

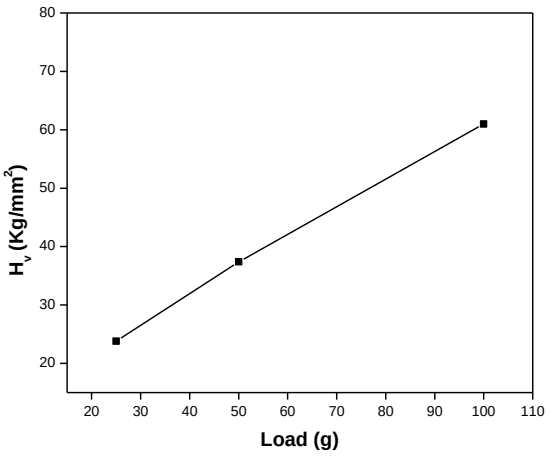

Figure 6: Variation of micro hardness number (H_v) with the applied load

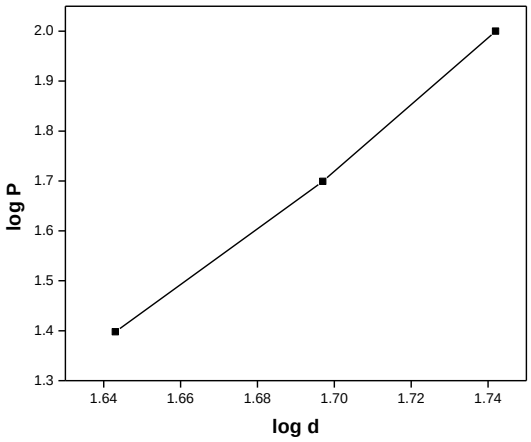

Figure 7: Variation of log P with log d for BBAU crystal

E. Dielectric Studies

The dielectric data obtained in the present study for BBAU crystal at various temperatures and at different frequencies are presented in the figure 8. It is observed that the dielectric constant (ε_r) decreases with frequency and increases with temperature. At lower frequencies, due to space charge polarization, ε_r value is usually higher. Strong temperature dependent variation of ε_r is attributed to dipolar polarization. However, the variation of the dielectric constant cannot be solely related to effects of temperature and frequency. The dielectric loss (tan δ) values obtained in the present study for BBAU crystal at various temperatures is provided in the figure 9. It is observed that dielectric loss also decreases with the the frequecy and increases with temperature. These results are similar to the results of dielectric studies of other samples of this work. Tables 2 and 3 tabulate the values of dielectric constant and dielectric loss respectively for BBAU sample for various frequencies and temperatures respectively.

Dependence of AC conductivity with log frequency for BBAU crystal is depicted in figure 10. A graph (figure 11) is drawn between ln σ_{ac} and 1000/T which gives a straight line. The slope of the straight line is equal to E/k from which the activation energy (E) was calculated as 0.194 eV. The activation energy gives an idea of the energy required to activated the charge carriers in the sample when electric field is applied.

Table 2: Values of dielectric constant for BBAU sample for various frequencies and temperatures

Temperature	Dielectric constant for frequencies (Hz)				
	10^2	10^3	10^4	10^5	10^6
45°C	10.32	9.82	8.83	8.02	7.52
50 °C	11.76	10.60	9.04	8.29	7.55
70 °C	15.66	13.99	10.75	9.18	8.77
80 °C	19.00	17.59	12.04	10.26	9.65
100 °C	21.06	19.02	15.58	11.18	9.87

Table 3: Values of dielectric loss for BBAU sample for various frequencies and temperatures

Temperature	Dielectric loss for frequencies (Hz)				
	10^2	10^3	10^4	10^5	10^6
45 °C	0.13	0.07	0.06	0.04	0.031
50 °C	0.15	0.07	0.07	0.05	0.028
70 °C	0.18	0.09	0.08	0.06	0.028
80 °C	0.22	0.11	0.09	0.07	0.032
100 °C	0.40	0.21	0.15	0.14	0.053

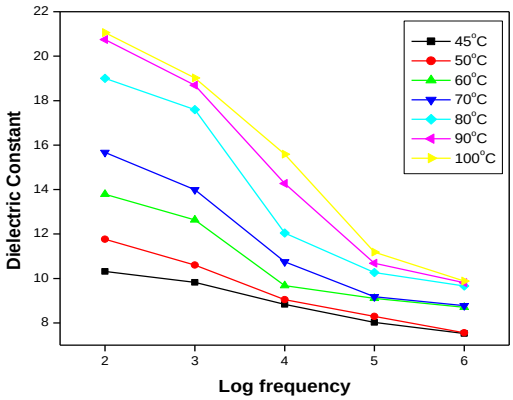

Figure 8: Variation of dielectric constant with frequency for BBAU crystal

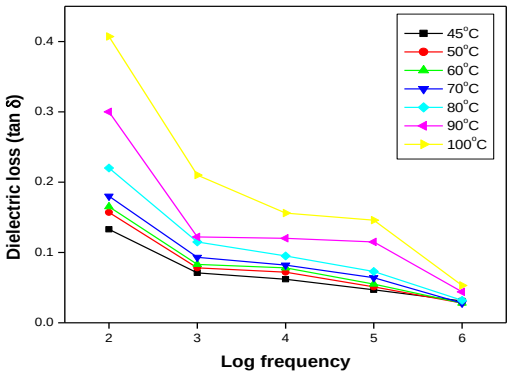

Figure 9: Variation of Dielectric loss with frequency for BBAU crystal

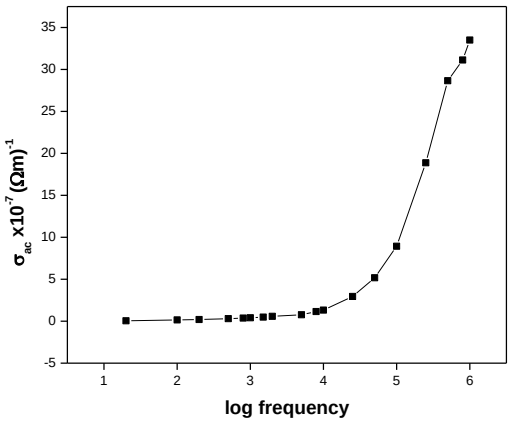

Figure 10: Dependence of AC conductivity with frequency for BBAU crystal

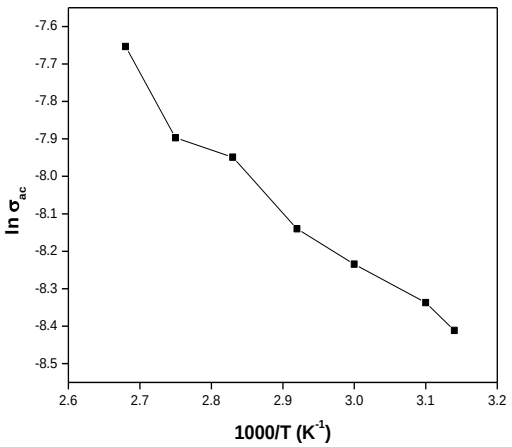

Figure 11: Plots of ln σ_{ac} versus 1000/T for BBAU crystal

CONCLUSION

Transparent, and colourless BBAU crystal were grown by solution method with slow evaporation technique. Single crystal XRD studies confirm the crystal structure of BBAU crystal to be orthorhombic. FTIR spectrum reveals the mode of vibrations of different molecular groups present in the grown BBAU sample. The cut-off wavelength of the grown BBAU crystal is found to be 235 nm from UV-visible-NIR spectral studies. Mechanical hardness studies reveal that Vickers hardness number steeply increases as the load increases for both the crystals. The dielectric constant and dielectric loss decrease with frequency and increase with temperature. The activation energies were calculated for both the crystals.

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