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Growth and Spectral Characterization of L-Valine Zinc Acetate Single Crystal

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Abstract: L-Valine zinc acetate (LVZA) was synthesized and its solubility was estimated in the solvent of double distilled water. Single crystals of LVZA were grown by slow evaporation solution growth technique. The cell parameters were obtained by single crystal X-ray diffraction study. Functional groups of LVZA were identified by FTIR analysis. UV-vis-NIR spectral studies showed the optical nature of LVZA. Kurtz powder technique revealed the SHG efficiency of LVZA. Thermal properties of the grown LVZA crystal were studied from TGA/ DTA and DSC spectrum. Vickers's mechanical hardness values were found for the grown crystal.

Keywords: Recrystallization, Solubility, Single crystal growth, X-ray diffraction, Nonlinear optical.

I. INTRODUCTION

The field of optoelectronic technology based on nonlinear polarization of molecular materials has attracted much interest [1, 2]. The second order nonlinear optical materials are widely used in the field of optoelectronic devices, laser communication and data storage technologies [3, 4]. Amino acids are interesting materials for NLO devices as they contain a proton donor carboxyl acid (COOH) group and the proton acceptor amine (NH_2) group with them [5- 7]. The dipolar nature of amino acids exhibits peculiar physical and chemical properties. The complexes of amino acids are extensively used in NLO applications [8- 11]. Almost all amino acids contain an asymmetric carbon atom. In particular bulk crystals of optically active amino acids possess wide optical transparency range in UV-vis spectral region, favourable mechanical hardness due to their zwitterionic nature and large hyperpolarizability [12-15].

In the recent years, efforts have been taken to synthesize semi organic system as they provide many structure and bonding schemes for molecular engineering of new materials. Particularly amino acid mixed organic and inorganic complex crystals have been grown, to improve the chemical stability, laser damage threshold and mechanical hardness [16-18]. Among amino acids, L-Valine (α-aminoisovalerate) is a branched chain amino acid, which has aliphatic non- polar side chain and has both a primary amino group and a primary carboxyl group. L-Valine is hydrophobic and can be formed from alanine by the introduction of two methyl groups in place of two H-atoms of the methyl group present on α- carbon atom. The carboxylate acid group donates its proton to the amino group, so in the solid state, amino acid exists as zwitterions, which create hydrogen bonds, which are very strong. Theoretical studies show that hydrogen bonds can strongly enhance the linear and nonlinear optical properties of bulk semi organic crystals [19, 20]. L- Valine formed salts with different organic acids and were reported [21-25]. In the present work, a systematic investigation was carried out on the growth of L- Valine zinc acetate [LVZA] crystal from aqueous solution by slow evaporation method and the grown crystals were subjected to single crystal X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, optical, thermal, mechanical and second harmonic generation (SHG) efficiency studies. The results of the studies are reported in this paper for the first time.

II. EXPERIMENT

A. Material Synthesis.

The starting materials L- Valine ($C_2H_{11}NO_2$) and zinc acetate ($Zn\ (CH_3COO)_2$) (analytical grade reagents) were taken in the equimolar ratio. The calculated amount of L- Valine was first dissolved in double distilled water. Then zinc acetate was slowly added to the solution with continuous stirring using magnetic stirrer. The prepared homogeneous mixture of solution was let to dry at room temperature. LVZA salt was synthesized according to the reaction:

$$(CH_3\text{-}CH\text{-}CH_3\text{-}CH\text{-}NH_2\text{-}COOH) + Zn\ (CH_3COO)_2 \rightarrow Zn\ [CH_3\text{-}CH\text{-}CH_3\text{-}CH\text{-}NH_3\text{-}COO]\ .\ [CH_3COO]_2$$

The purity of the synthesized salt was improved by the successive recrystallization process. Care was taken during heating of the solution and a maximum temperature of 50° C was maintained in order to avoid decomposition.

B. Solubility

The solubility of LVZA in double distilled water was determined as a function of temperature, range 30- 50°C. To determine the equilibrium concentration, the solution LVZA was prepared using double distilled water as the solvent. The solution was maintained at a constant temperature bath and continuously stirred to achieve homogeneous temperature and concentration throughout the volume of the solution. On reaching the saturation, the solute content of the solution was analyzed gravimetrically [26] and this process was repeated for every temperature. The solubility curve of LVZA is shown in Fig. 1 which shows the solubility increases with increase of temperature and LVZA has positive temperature coefficient of solubility. Hence LVZA is suitable for the growth by slow evaporation method.

C. Single Crystal Growth

Saturated solution was prepared (pH= 5.08) using recrystallized salt of LVZA with double distilled water as solvent at 35°C temperature. The prepared solution was filtered using Whatmann 41 filter paper to remove the suspended impurities. The solution was taken in beakers and covered with perforated papers. The covered beaker with saturated solution was kept in constant temperature bath (CTB) at 35°C with accuracy of ±0. 01°C. LVZA single crystal was grown by slow evaporation technique and harvested in a growth period of 25 days and is shown in Fig. 2.

III. CHARACTERIZATION

Single crystal X- ray diffraction analysis was carried out using an ENRAF CAD- 4 diffractometer with MoKα (λ= 0. 71073Å) radiation at room temperature to estimate the lattice parameter values. The Fourier transform infrared (FTIR) spectrum of LVZA crystals was recorded in the range 400- 4000 cm^{-1} employing a Perkin- Elmer RXI spectrometer by the KBr pellet method in order to confirm the presence of functional groups in the grown crystal. UV-vis- NIR spectrum of LVZA crystal was recorded using Perkin Elmer- lambda 35 UV-vis spectrophotometer in the range of 190-1100nm. Second harmonic generation efficiency was measured using Kurtz and Perry powder technique. Micro hardness measurements were made using Shimadzu HMV-2 micro hardness tester fitted with a Vickers diamond pyramidal indenter. Thermal analysis was carried out using SDT Q 600V 8.3 build 101 simultaneous DTA/ TGA, DSC analyzer in the nitrogen atmosphere.

IV. RESULTS AND DISCUSSION

A. Single crystal X-ray Diffraction Analysis

Lattice parameters of LVZA crystal obtained form this analysis are compared with L- Valine [27] and shown in Table 1. From this study it was found that the LVZA crystallizes in monolithic system (β=112.73°). The volume of the cell is 792$Å^3$.

B. FTIR Spectral Studies

The recorded FTIR spectrum of LVZA is shown in Fig. 3. Considering the molecular structure of L-Valine, the vibrations of crystalline L-Valine zinc acetate may be arised due to internal vibration of functional groups NH_3^+, CH, CH_3 and COO^-. The presence of broad band in high wave number region indicates the presence of hydrogen bonds [29]. A broad strong absorption in the region 3400- 2100 cm^{-1}corresponds to the NH_3^+ ion of the amino acid. Generally N- H and O- H bonds participate in hydrogen bonding. In LVZA crystal, the valine molecule is protnated at amino group (NH_3^+) and deprotonated at the carboxylate group (COO^-). The protonation of amino group can be proved because of the presence of strong band at 1611 cm^{-1} (asymmetric deformation of NH_3^+). The asymmetric stretching vibration of NH_3^+ion for L-Valine appeared at 3089 cm^{-1}. This band is shifted in LVZA at 3060 cm^{-1}. Moreover, presence of absorption bands at 2632, 2431, 2213, 2019 and 1896 cm^{-1} can be attributed to the overtone and combination bands of NH_3^+ bending and C- H stretching vibration overlapping. The presence of COOH is indicated by a sharp absorption band at 1706 cm^{-1}, which is due to the C= O stretching mode of COOH group [30].

The absorption bands occurred at 1464 and 1381 cm^{-1} due to COO^- symmetric stretching of LVZA showed the zwitterionic nature of amino acids. These bands are shifted from 1425 and 1396 cm^{-1} of L-valine spectrum. The existence of CH_3 group is evident from 2933 cm^{-1} (CH_3 asymmetric stretching) and 1242 cm^{-1}(CH_3 deformation).The presence of CH group can be assigned from the bands at 851 and 629 cm^{-1} (C-H bending). The observed wave numbers obtained from the recorded spectrum are compared with L- Valine [27, 28] and assigned in Table 2.

C. Linear Optical Studies

The transmission spectrum of the LVZA recorded in the range 190- 1100 nm is shown in Fig. 4. There is no absorption in the entire UV and visible region. The lower cut- off wavelength for LVZA is observed below 210 nm.

D. Second Harmonic Generation Efficiency

The SHG efficiency of LVZA was measured by the Kurtz and Perry powder technique [31]. The second harmonic output was generated by irradiating powder sample by a pulsed Laser light. The laser source is an Nd- YAG laser with a pulse width of 8 ns and a repetition rate of 10 Hz. The incident laser power was chosen as 2.4 mJ/P. The NLO nature of the sample was confirmed by the emission of green radiation (λ= 532Å) which was finally detected by a photomultiplier tube (PMT) and displayed on the oscilloscope (CRO). The optical signal incident on the PMT was converted into voltage output at the CRO. The output second harmonic signal of 48mV for LVZA crystal sample and 35 mV for standard KDP sample were found for the same input energy. Hence the measured SHG efficiency for LVZA sample was about 1.37 times, as that of KDP.

E. Thermal Analysis

Thermal stability of the LVZA was studied by TGA, DTA and DSC analyses. The spectrum was recorded in the temperature range 10-1200° C. The recorded TGA/DTA spectra of the LVZA sample are shown in Fig. 5. Heating was carried out at a rate of 20° C/min. The initial mass of the material subjected to analysis was 2.9970 mg and the final was left out after the experiment was only o. 3630% of the initial mass at temperature of about 1100°C indicating bulk decomposition occurring into LVZA crystals. From the TGA curve, the thermal stability of the sample is realized up to 163°C and there after the material shows loss in weight due to the molecules, which are loosely bounded to the metal ion. The major 70% of weight loss between 208°C to 279°C is due to the liberation of volatile substances.

It is observed from DTA curve, that the material undergoes exothermic transition at about 217°C where the decomposition starts. The material is fully decomposed at an irreversible endothermic transition at about 286°C. It is inferred that the melting point of the material takes place in the vicinity of 286°C. The sharpness of the endothermic peak shows good degree of crystallinity of the grown LVZA. From DSC spectrum, the melting point of the LVZA crystal is observed at 286°C which is comparable with DTA result. The observed DSC spectrum of the LVZA crystal is shown in Fig. 6.

F. Micro Hardness Studies

Hardness of a material is a measure of the resistance it offers to local deformation [32]. Microhardness studies were carried out on LVZA single crystals using micro Vickers's hardness tester, fitted with a Vickers diamond pyramidal indenter. The indentations were made for loads 25- 100g. Several trials were performed for the same load and the average diagonal length was taken for each load. The indentation time was 10 s. Vickers micro hardness values were calculated by the relation,

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

Where P is the applied load in kg and d is the mean diagonal length of the indenter impression in mg. A graph was plotted between the hardness number H_v and the applied load P and the graph is shown in Fig. 7. It is observed from the graph that the harness value increases with the increase of the applied loads. The behaviour of increasing microhardness with the load known as reverse indentation size effect (RISE) [33].

V. CONCLUSION

New nonlinear optical material L-Valine zinc acetate was synthesized and good optical quality single crystals of LVZA were grown using a slow solvent evaporation technique. Single crystal X- ray diffraction study revealed that the LVZA crystal belongs to monolithic system and the unit cell parameters of LVZA were obtained. The functional groups present in LVZA were confirmed by FTIR and the vibrational frequencies assigned. In the UV-visible optical spectrum, it is evident that the LVZA crystal has a wide transparency range in the entire visible range. The SHG efficiency of LVZA is 1.37 times that of KDP. TGA, DTA and DSC showed the thermal stability of the grown LVZA crystal. Microhardness studies of LVZA reveal the reverse indentation size effect.

VI. ACKNOWLEDGEMENT

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FIGURE CAPTIONS

1) Fig. 1 : Solubility curve of LVZA in water
2) Fig.2 : Photograph of LVZA crystal
3) Fig.3 : FTIR spectrum of LVZA crystal
4) Fig. 4 : UV- Vis absorption spectrum of LVZA
5) Fig. 5 : TG/ DTA curve of LVZA crystal
6) Fig. 6 : DSC spectrum of LVZA
7) Fig. 7 : Hardness values H_v versus load P

Table Captions

1) Table 1 Lattice parameters of LVZA and L- Valine
2) Table 2 Assignment of FTIR band frequencies (cm^{-1}) for LVZA and L- Valine

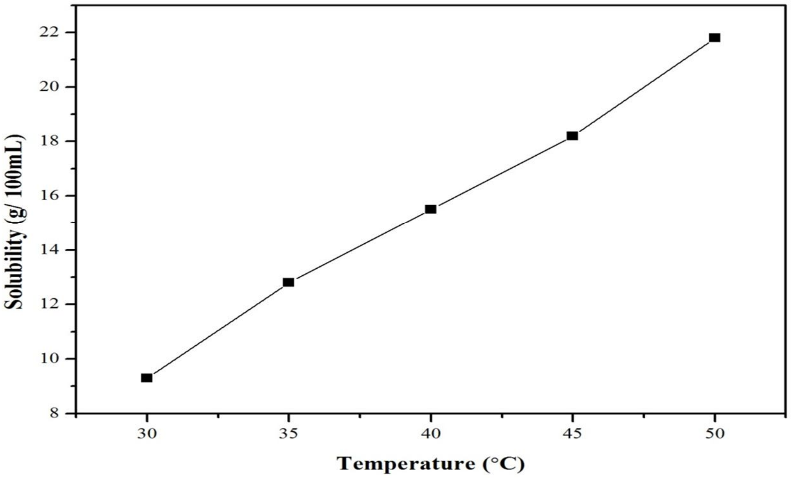

Fig. 1 : Solubility curve of LVZA in water

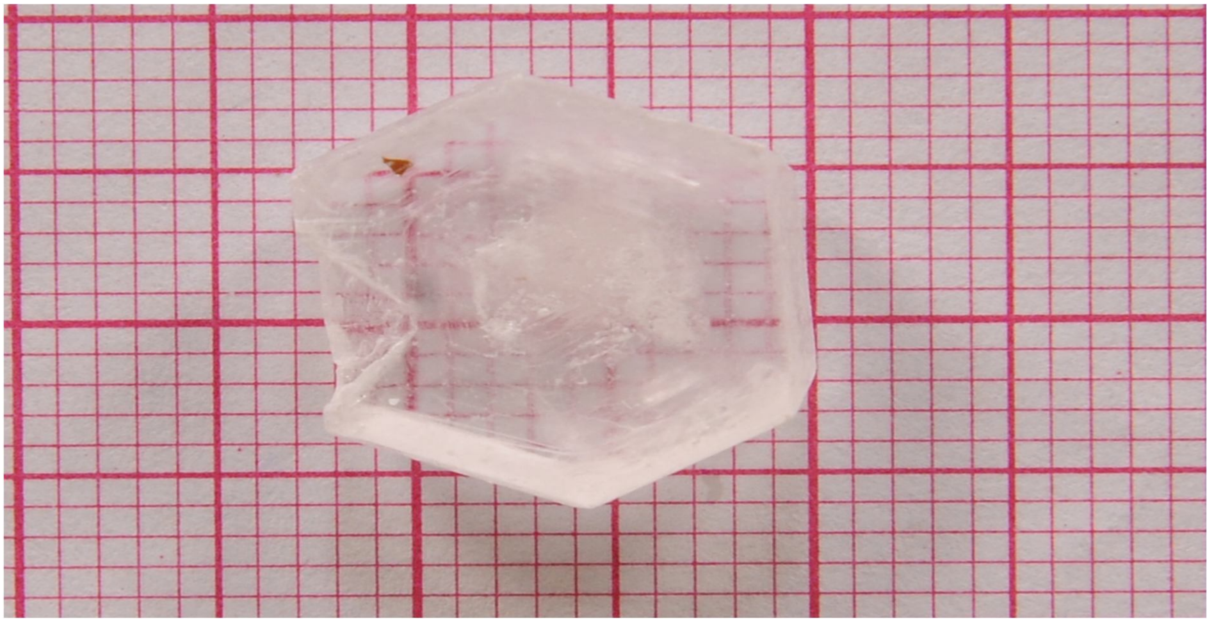

Fig.2 : Photograph of LVZA crystal

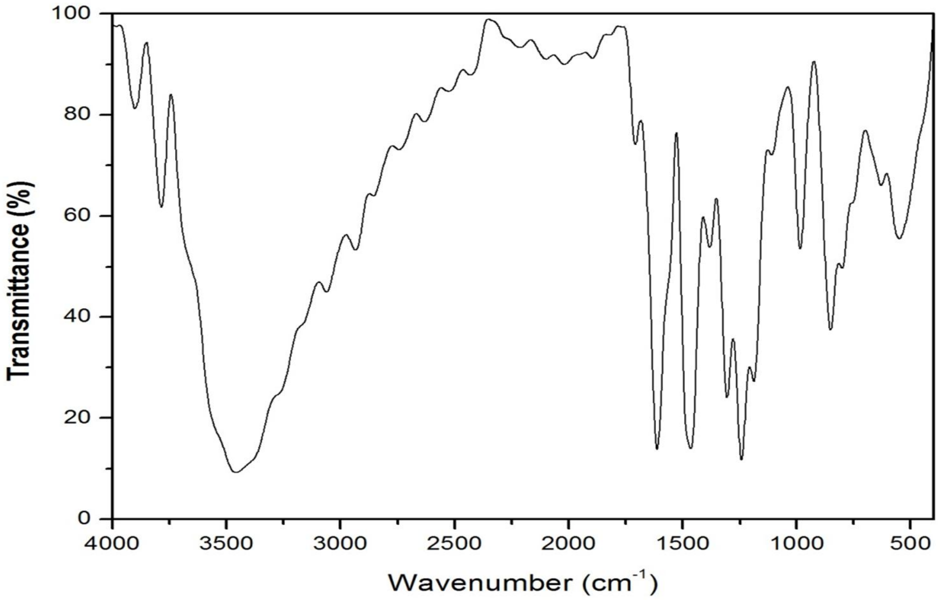

Fig.3 : FTIR spectrum of LVZA crystal

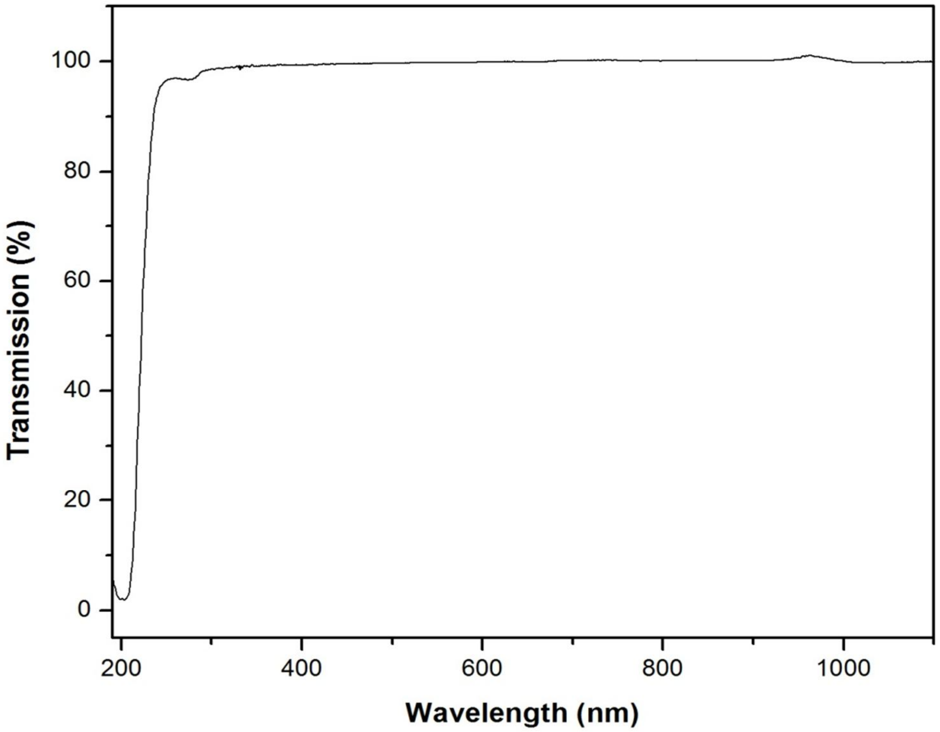

Fig. 4 : UV- Vis absorption spectrum of LVZA

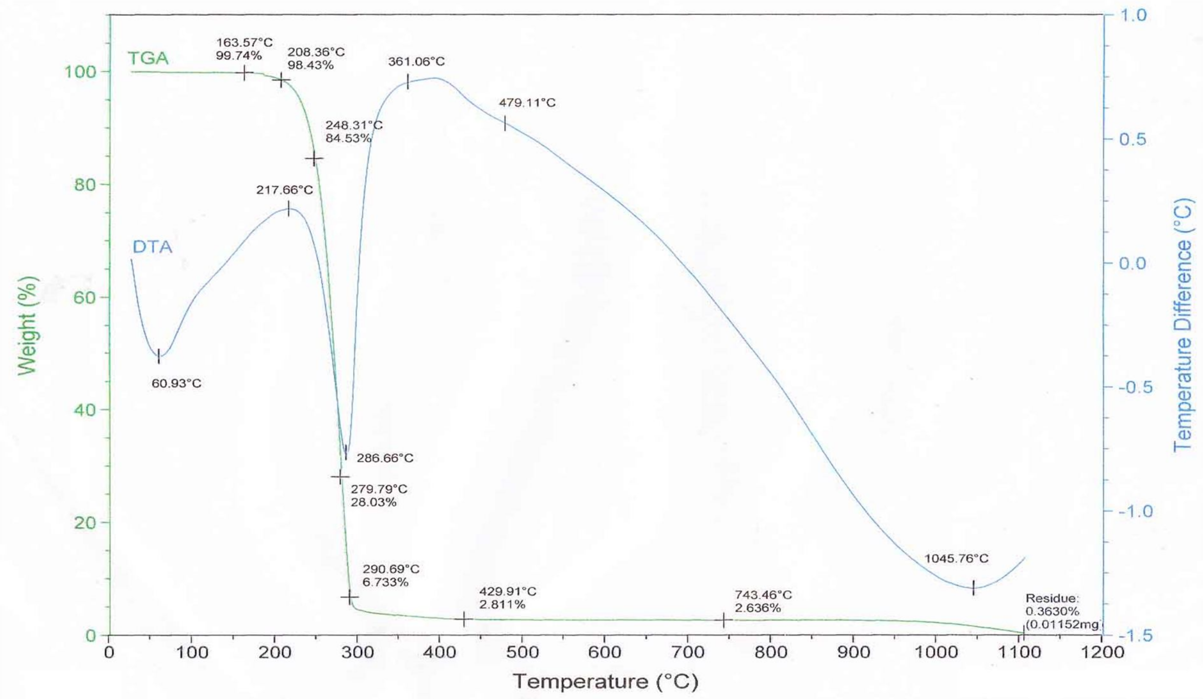

Fig. 5 : TG/ DTA curve of LVZA crystal

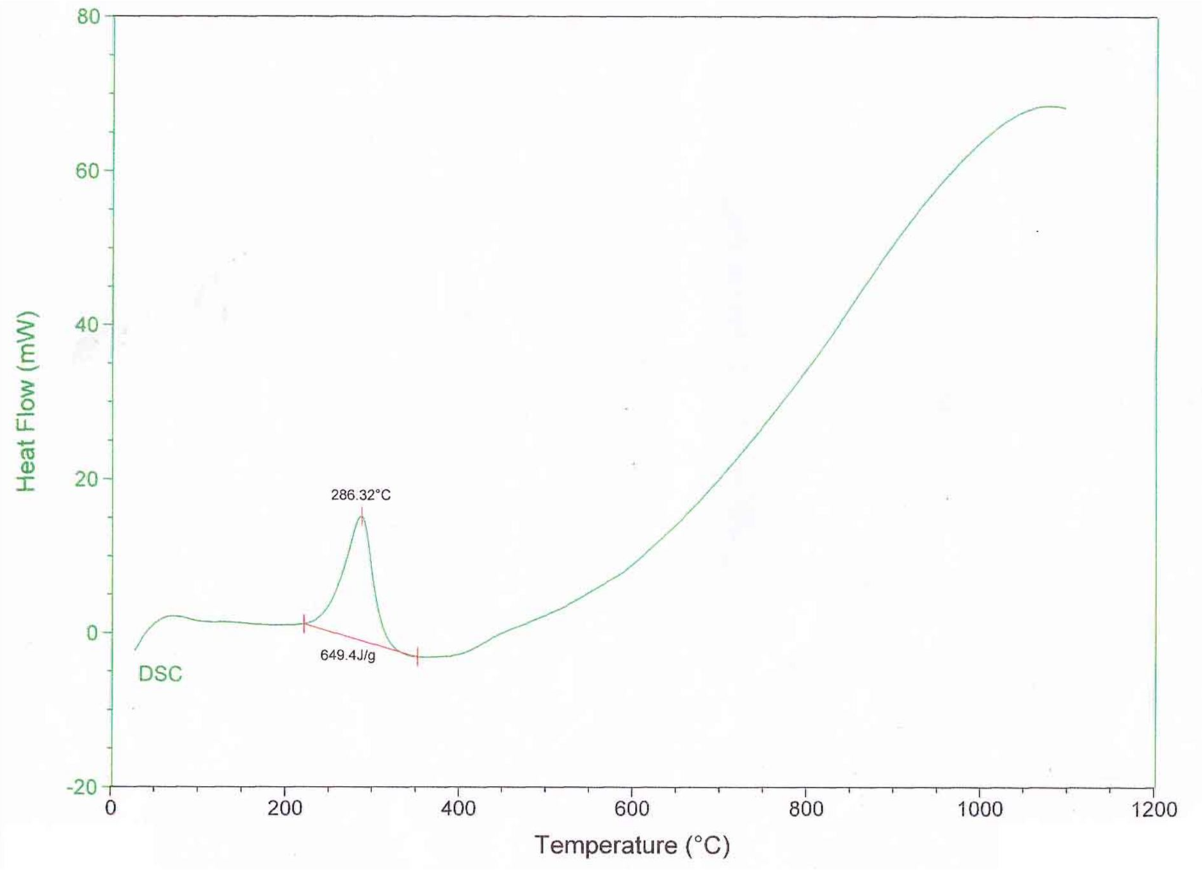

Fig. 6 : DSC spectrum of LVZA

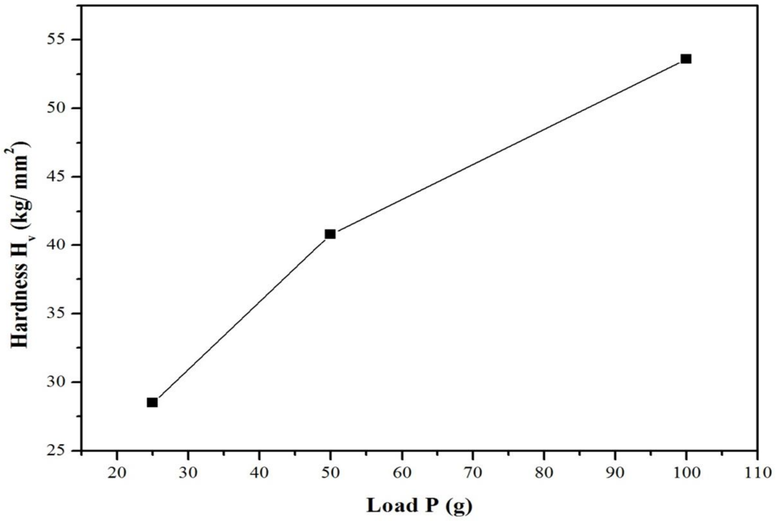

Fig. 7 : Hardness values H_v versus load P

Table 1 Lattice parameters of LVZA and L-Valine

Lattice Parameters	LVZA Present work	L- Valine [27]
a (Å)	10.02	9.701
b (Å)	6.43	5.261
c (Å)	13.33	11.953
β(°)	112.73	90.66

Table 2 Assignment of FTIR band frequencies (cm^{-1}) for LVZA and L-Valine.

Wave number (cm^{-1})		Assignments
LVZA	LValine[27,28]	
3060	3089	Asymmetric stretching of NH_3^+
2933	2975	Asymmetric stretching of CH_3
1706	--	Stretching of C=O
1611	1613	Asymmetric deformation of NH_3^+
1464	1425	Symmetric stretching of COO^-
1381	1396	Symmetric stretching of COO^-
1305	1329	Stretching of C-O
1242	1271	Deformation of CH_3
1187	1178	Stretching of C-C
1109	1140	Stretching of C-C
984	949	Rocking of CH_3
851	824	Bending of C-H
629	664	Bending of C-H
549	543	Rocking of COO^-