



# Growth, structural, spectral, optical, mechanical and thermal properties of L-Valine Added Sulphamic acid Single Crystals

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## Abstract

L valine in added sulphamic acid crystals was grown by slow evaporation technique. The harvested crystals were subjected to various characterizations for revealing its structural, optical, mechanical and thermal properties. Powder X – ray diffraction expose that LVSA crystallizes in an orthorhombic structure. FTIR techniques have verified its structural identification. The EDAX analysis confirmed the presence of carbon in the grown crystal. The surface morphology of crystals was studied. Optical absorbance and transmittance spectrum recorded and exhibited that this crystals has good transparency in the visible region. From absorbance spectrum the optical band gap energy is found to be 3.5ev. The mechanically soft nature of the crystal was estimated by Vickers hardness measurement. The stability of LVSA crystal was ascertained from thermo gravimetric and differential thermal analysis.

**Keywords:** Sulphamic acid, L-valine, XRD, FTIR, EDAX, SEM

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## 1. Introduction

Non linear optical materials play an important role in the area of photonics that involves the use of photon in the same way electronic applications use the electron. Optical devices have more advantages than electronic devices. The data transmitted optically can travel longer distances in a fraction of the time due to the speed of light which is about ten times greater than that of electricity. Due to this fact the rapid development of optical communication system has led to a demand for non linear optical materials of high structural and high optical quality. Nowadays nonlinear optical materials are having potential applications in the area of telecommunications and optical storage devices [1, 2]. Amino acids and their

complexes belong to a family of organic materials that have enormous applications in the field of non linear optics [3-6]. Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid ( $\text{COO}^-$ ) group and the proton acceptor amino ( $\text{NH}_3^+$ ) group [7].

Sulphamic acid is the mono amide of sulphuric acid, which is strongly soluble in water and exhibits zwitter ionic forms and its derivatives have wide industrial applications as anti corrosive agent and cross linking agent for polymers [8, 9]. In the present work L-Valine added Sulphamic acid was synthesized and the growth and characterization of L-Valine added sulphamic acid single crystal was reported.



## 2. Experimental Methods

The crystals of L-valine added sulphamic acid were grown by slow evaporation technique using the AR grade sulphamic acid and L-valine powders. To grow L-valine added sulphamic acid crystal the AR grade sulphamic acid and L-valine in the molar ratio 3:1 were taken and dissolved in deionized water. The dissolved mixture was stirred well using magnetic stirrer for few hours at room temperature until well liquefied. The saturated solution was filtered

using a filter paper to remove any non-miscible and unstirred chemical. The filtered transparent solution was shifted to crystal growth vessels, enclosed by aluminum foil sheet with few punched holes and stored in a dust free atmosphere. The solution was permitted to crystallization at room temperature. Good transparent and colorless crystals were collected after 20 days. Fig. 1 shows the photograph of the grown L-valine added sulphamic acid (named as LVSA) crystals.



Figure 1. Photographs of the grown LVSA crystal

## 3. Results and discussions

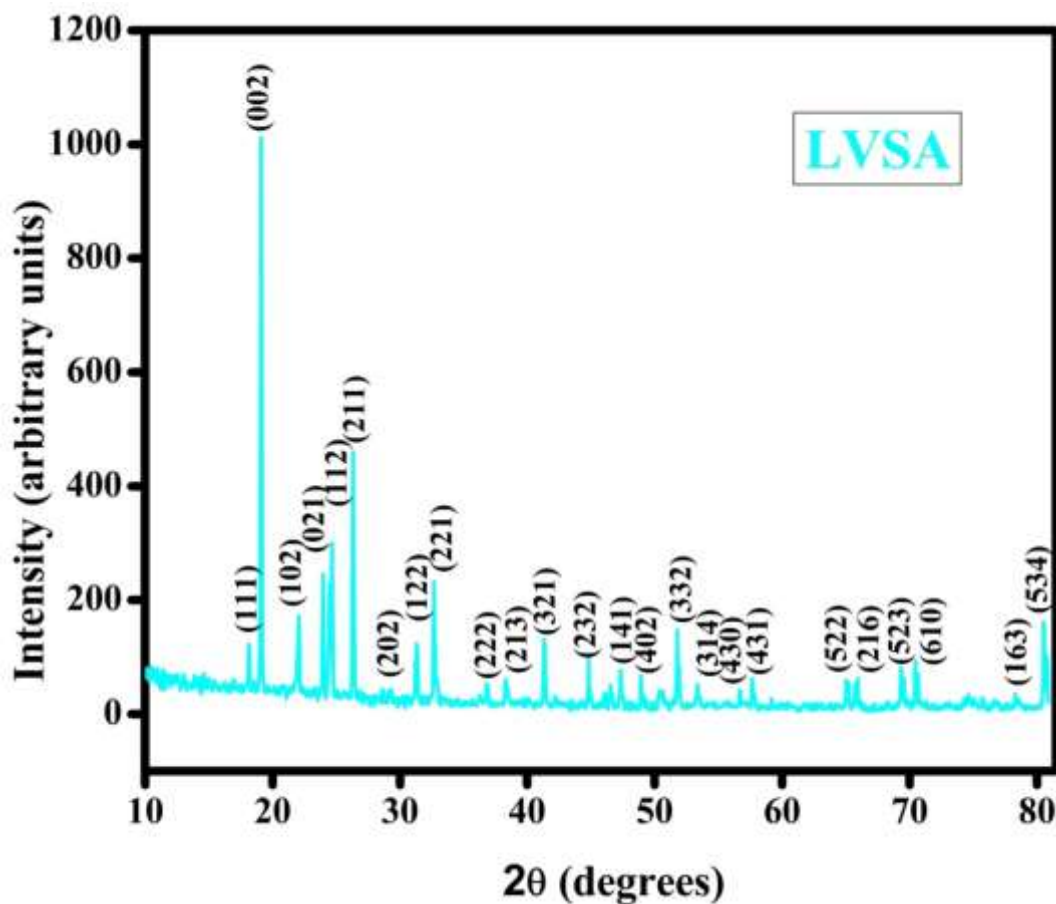
### 3.1. Powder X-ray diffraction

Figure. 2 shows the recorded powder XRD pattern of as grown

L-valine added sulphamic acid crystals. The diffraction peaks in the XRD profile was matched to the standard JCPDS data. From the standard pattern, it was found that the observed XRD pattern of the grown crystals was well suited to the orthorhombic crystal system of sulphamic acid (JCPDS card no : 70-0060). In L-valine added samples the crystallinity of the sample was increased and the most intense peak was along (002) direction. Also, the intensity of the strongest peak (002) was decreased slightly whereas

the intensity of other peaks also decreased. This revealed that the addition of L-valine improved the crystalline nature of the sample and also the growth axis was enhanced along (002) direction. The change in the relative intensity of the various peaks was also noticed which proposed the successful incorporation of L-valine in the pure sulphamic acid. Moreover, no impurity peaks have appeared. Hence the grown crystals were phase pure. The unit cell parameters were calculated and tabularized. Using unit cell software package, the tabulated lattice parameters and structure were found to be in good accordance with the previous results of sulphamic acid [10-13].





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Figure 2. Powder X-ray diffraction patterns of LVSA crystal

Table 1. Structure and lattice parameters of LVSA crystal.

Crystal	Structure	a(A°)	b(A°)	c(A°)	$\alpha=\beta=\gamma$	Volume(A <sup>3</sup> )
LVSA	Orthorhombic	8.1217	8.0833	9.2496	90°	607.2434



### 3.2. Fourier Transform Infrared Analysis

The FT-IR spectra of the grown crystal of LVSA are shown in Fig. 3. From the spectra, it is clear that the band due to  $\text{NH}_3^+$  mode of bonding was noticed at frequency of  $3130\text{ cm}^{-1}$  and  $2873\text{ cm}^{-1}$ . The band observed at  $2449\text{ cm}^{-1}$  and  $2026\text{ cm}^{-1}$  were due to tri bands overtones/combinations of hydrogen bonded OH bending modes. The bands seen at  $1807\text{ cm}^{-1}$  and  $1444\text{ cm}^{-1}$  were due to deformation of  $\text{NH}_3^+$  mode of vibration. The vibration bands observed at  $1278\text{ cm}^{-1}$  was due to degenerated  $\text{SO}_3^-$  stretching, whereas at  $1073\text{ cm}^{-1}$  was due to symmetric  $\text{SO}_3^-$  stretching. The rocking mode vibration  $\text{NH}_3^+$  was noticed at  $1002\text{ cm}^{-1}$  which

verified the formation of zwitterions in LVSA crystal. [14]. The N-S stretching vibration was observed at  $695\text{ cm}^{-1}$  and the band that occurred at  $536\text{ cm}^{-1}$  was due to degenerated  $\text{SO}_3^-$  deformation [15]. All the IR bands that observed in the grown crystals were in good agreement with earlier reports and were comparable with theoretically calculated bands [14, 16]. Table 2 shows the vibrational assignment of LVSA crystal. However in comparing with pure SA, L-valine added crystals almost all the modes were appeared. But the intensities were drastically decreased which revealed that there may be subtle change in the geometry of the sub lattice.

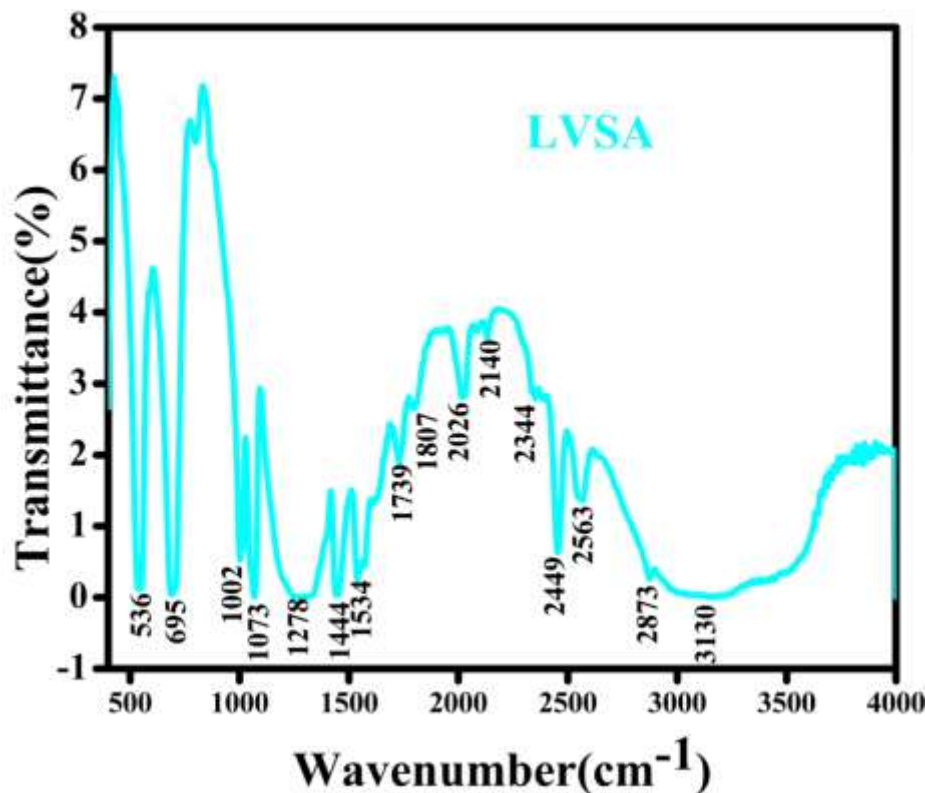


Figure 3. FTIR spectra of LVSA crystal

Table 2. Vibrational assignment of L-valine added SA single crystal

Wave number( $\text{cm}^{-1}$ )	Assignment



536	Degen. SO <sub>3</sub> <sup>-</sup> deformation
695	N-S stretching
1002	Rocking mode NH <sub>3</sub> <sup>+</sup>
1073	Symmetric SO <sub>3</sub> <sup>-</sup> Stretching
1278	Degen.SO <sub>3</sub> <sup>-</sup> stretching
1444	Sym. NH <sub>3</sub> <sup>+</sup> deformation
1534	Degen. NH <sub>3</sub> <sup>+</sup> deformation
1807	Symmetric NH <sub>3</sub> <sup>+</sup> deformation
2026	N-H Stretching
2449	S-H Stretching
2873	Symmetric NH <sub>3</sub> <sup>+</sup> Stretching
3130	Degen.NH <sub>3</sub> <sup>+</sup> Stretching

### 3.3 Morphology and compositional analysis

The surface morphology of as grown L-valine added sulphamic acid crystals was examined using scanning electron microscope and was shown in Fig. 4. The SEM image revealed that the particles were in non-uniform size and displayed agglomeration along with voids. On close examination it was noticed that in L-valine added crystals the crystallinity was improved since the size of the crystals were increased and the voids were reduced. Further the small agglomeration was removed and crystalline nature can be viewed clearly.

The chemical composition of the grown crystal was derived from the micro analytical technique known as energy dispersive X-ray analysis. Figure 5. Shows the EDAX spectra of LVSA crystals. The presence of elements like oxygen, nitrogen, sulphur and carbon in L-valine added sulphamic acid crystal confirmed that the added elements are incorporated in the crystal lattice. From EDAX results the successful addition of L-Valine in to SA crystals was confirmed. The elemental compositions were tabulated in Table 3.

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**Table 3. Elemental composition of LVSA**

Element	Atomic weight (%)	Molecular weight (%)
Sulphur	5.78	11.51
Oxygen	63.88	63.49
Nitrogen	19.02	16.55
Carbon	11.33	8.45



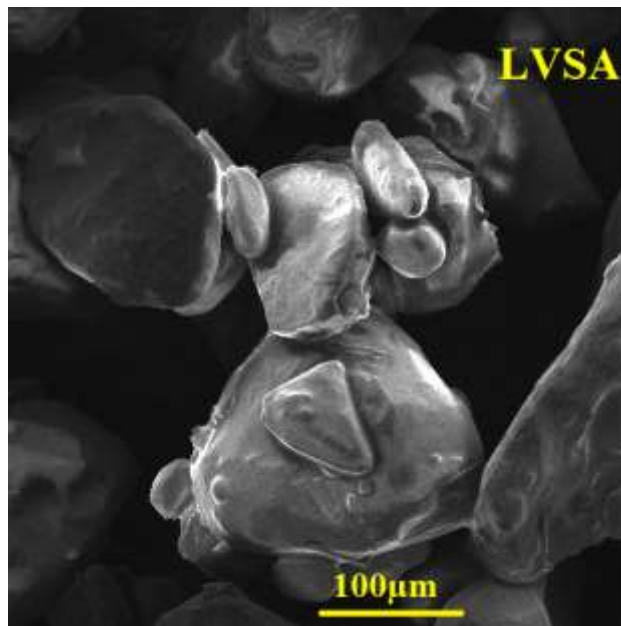


Fig. 4 SEM analysis of LVSA crystals

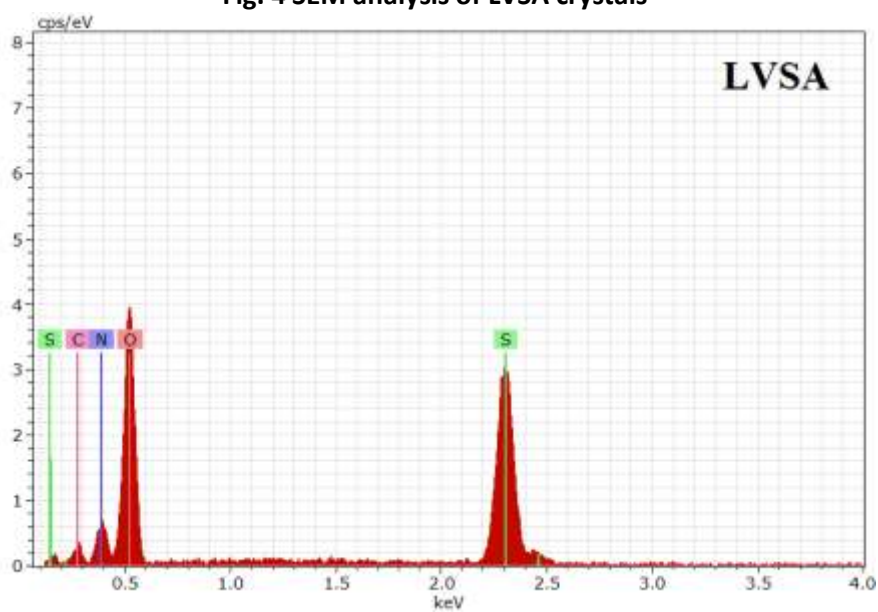


Fig. 5 SEM analysis of LVSA crystals

### 3.4 UV-VIS studies

It is very substantial to know the optical transparency of the grown crystals since they are used in several optoelectronic device applications. The Ultraviolet-Visible-near infrared spectroscopic measurements were done and the graph was shown in Fig. 6. It is clear from the figure that the grown crystals have transparency of 99%. The transparency of the LVSA crystals was found to increase due to

increase in crystalline nature. The reduction of transmittance in SA crystals may be because of the scattering from the point and line defects as reported by M. Senthil pandian et al [17]. From Fig. 7 it was found that the lower uv-cut off wavelength for the SA crystal was 235nm and percentage of absorption is high for L-valine added sulphamic acid in comparison with pure sulphamic acid and it could be due to the influence of L-valine.[18]. The tau's plot



analysis was carried out to find the energy band gap values and was shown in Fig. 8. The

obtained optical band gap of L-valine added sulphamic acid was 3.5eV.

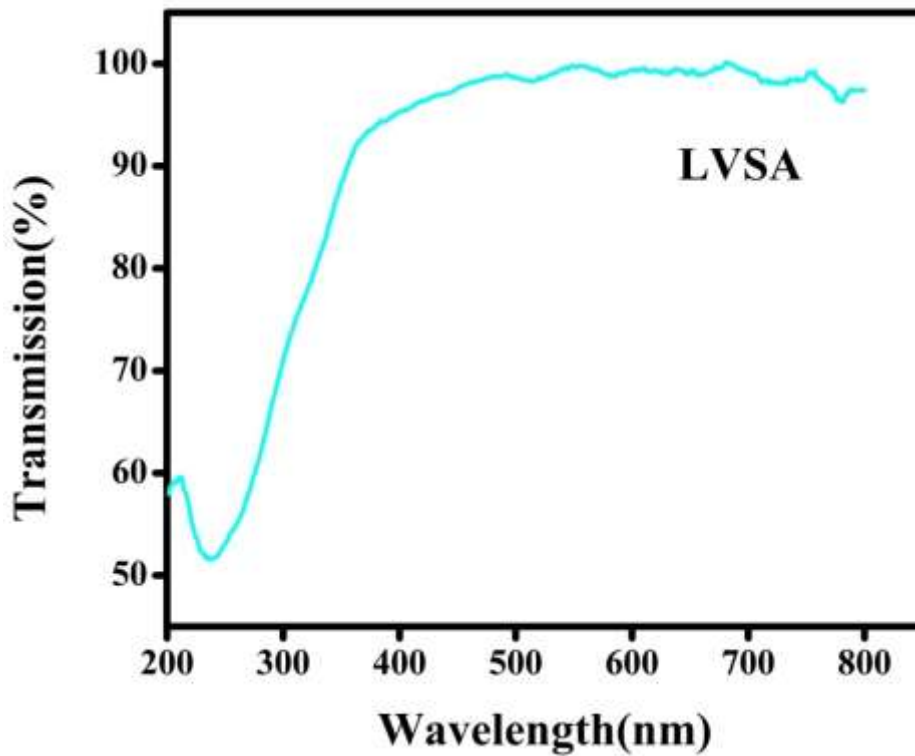


Fig 6. UV Transmission spectra of LVSA.

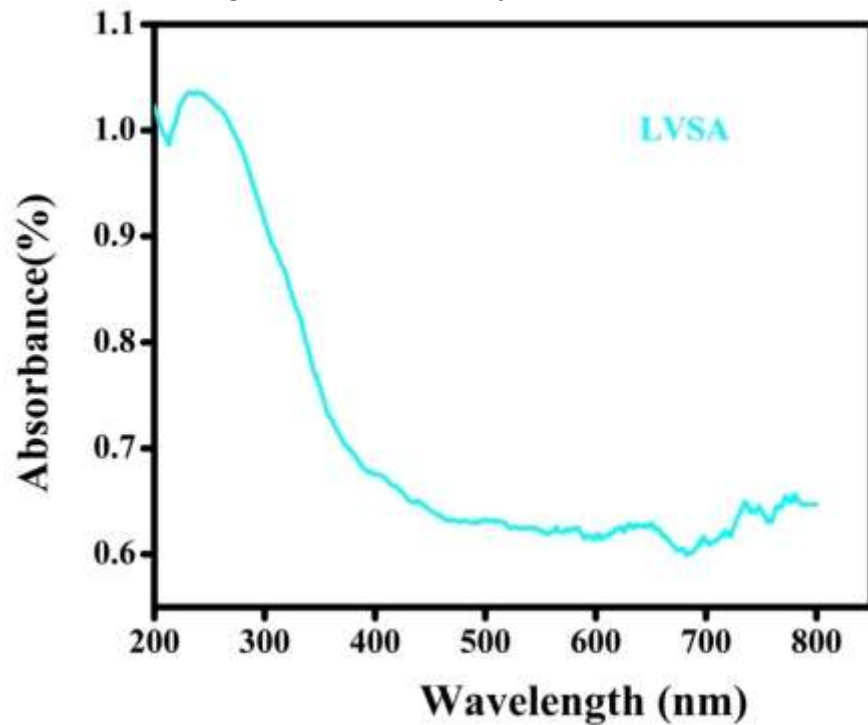


Fig 7. UV Absorption spectra of LVSA.



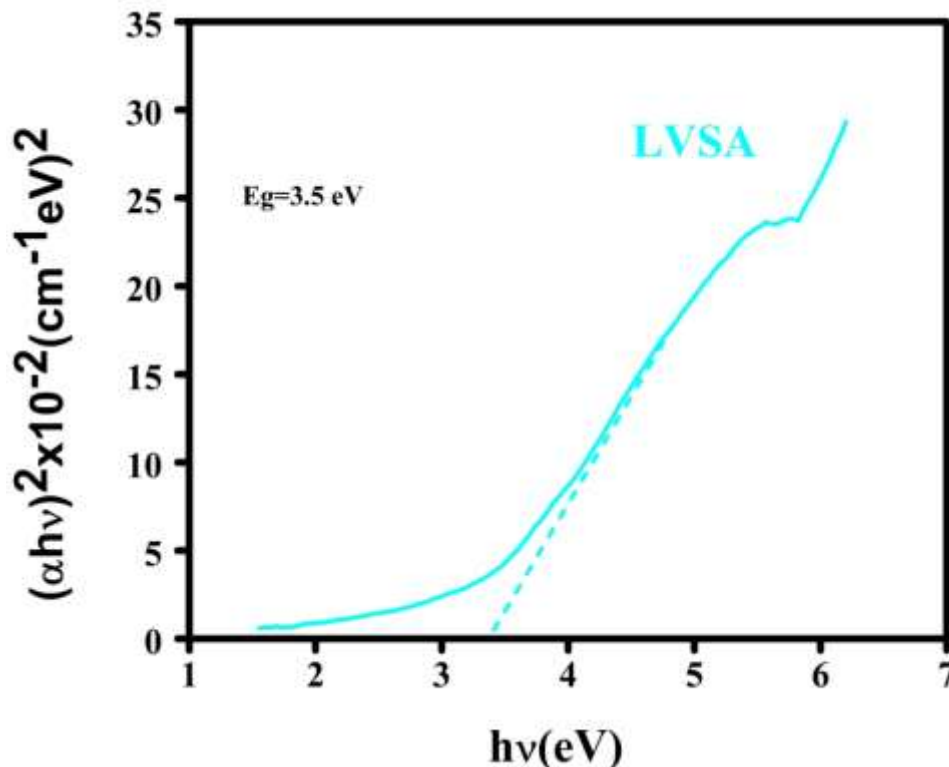


Fig 8. Tauc's plot for LVSA crystal.

**3.5 Vickers's Hardness Test:**

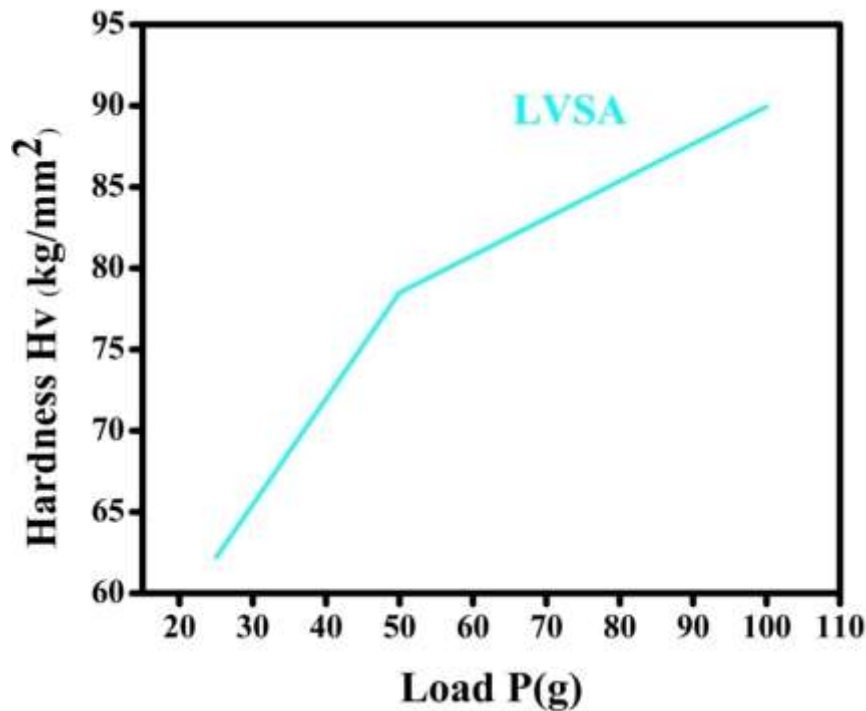
The applications of the crystals are dependent on optical performance as well as good mechanical behavior [19, 20]. Vickers micro hardness measurements were done for the LVSA crystals at room temperature with the load ranging from 25g to 100g. The diagonal lengths of the indentation (d) was calculated in  $\mu\text{m}$  for various applied loads (p) in g. Vickers hardness number was determined using the relation

$$H_v = 1.8544P/d^2 \text{kgmm}^{-2}$$

Fig. 9 shows the plot between load and hardness number. From the plot, it was noticed that the hardness number increased with increase in load up to 100g. No crack has

been observed till 100g. The presence of L-valine played an important role in increasing the hardness property of the SA crystal. Similar behavior has been reported by Arumugam et al and Babu et al [21, 11]. The work hardening coefficient was studied from the plot of  $\log p$  versus  $\log d$ , and the results are shown in Fig. 10. Least square fitting gives a straight line, which are in good agreement with Meyer's law. The value of n is calculated from the slope of the graph. According to Hanneman and onitsch [22] n should lie between 1 and 1.6 for hard materials and above 1.6 for soft materials. For LVSA crystal it was found to be above 1.6. Hence this crystal belongs to soft materials group.





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Fig.9 Plot of Load (P) Vs Hardness number (Hv) for LVSA crystal

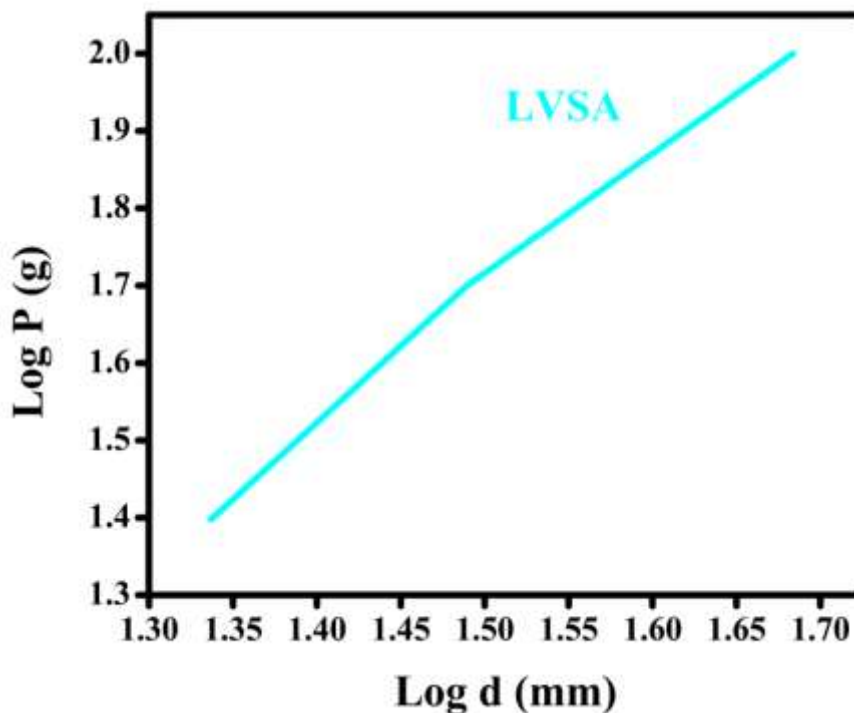


Fig. 10. Log p Vs Log d for LVSAcrystal.

### 3.6 TG-DTA Analysis

The phase transition of the grown crystal, water of crystallization and different stages of decomposition can be determined from TGA/DTA analysis [23]. TGA/DTA analysis of L-valine added SA was shown in Fig. 11. It was

noticed that there is no weight loss of up to 285°C. A sudden drop was observed from 285°C to 465°C. This is related to the decomposition point of the material. Total decomposition of the crystal takes place at temperature 465°C for LVSA crystal. Hence these compounds have



good thermal stability up to 285°C for LVSA crystals. Hence we can say that the grown

crystals are suitable for applications with working temperature up to 285°C.

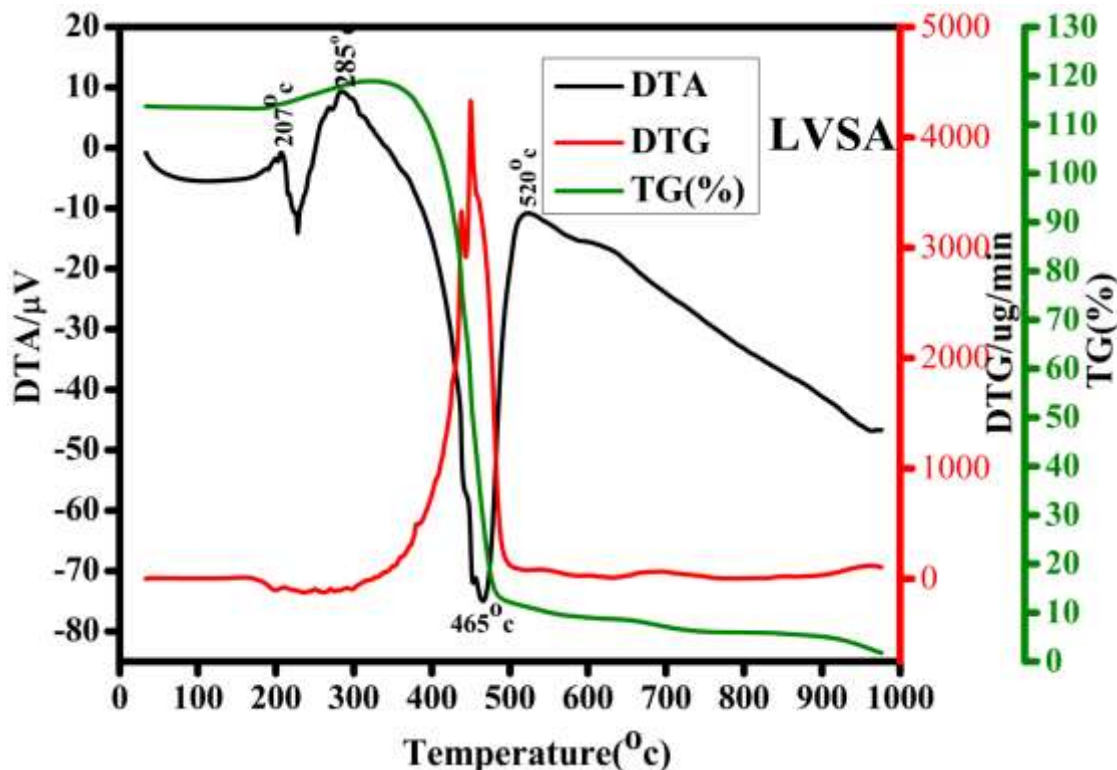


Fig.11.TG-DTA curves of LVSA crystal

#### 4. Conclusion

The L-valine added sulphamic acid crystals have been grown by slow evaporation technique at room temperature. Powder X-ray diffraction studies revealed orthorhombic crystal structure and lattice parameters were also evaluated. A small change in the lattice parameters and volume of the crystals was noticed when L-valine is added to sulphamic acid. The FTIR spectroscopic analysis verified that there is no phase change upon addition of L-valine to sulphamic acid. All the vibrational modes were present with slight deviation in the peak position. The morphological and compositional analysis proved that, on addition of L-valine, the crystallinity was improved and the presence of carbon was identified. The optical study showed that the transparency is very high compared to SA. The value of band gap was found to decrease with the addition of L-valine. The mechanical strength was enhanced

while adding L-valine and the crystal goes to a soft material group. TG-DTA analysis showed that the grown crystals have good thermal stability up to 295°C.

#### 5. References

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