Growth and Characterization of L – proline Added Sulphamic acid Single Crystals

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Abstract

Slow evaporation technique has been used to grow pure and L-proline added sulphamic acid single crystals. Unit cell parameters and structure of the grown crystal were confirmed by powder XRD analysis and it was found that it crystallized in an orthorhombic structure. The functional groups of the grown crystal were found by FTIR and RAMAN analysis. The surface morphology and the presence of all constituent elements were confirmed by SEM and EDAX analysis. The optical transmittance, absorbance and bandgap energies of the grown crystal were studied by UV-Vis-NIR spectral analysis. The mechanical strength of the grown crystal was identified by Vickers microhardness test. Thermal bebaviour of the grown crystals was identified from Thermogravimetric Analysis (TGA) and Differential Thermogravimetric Analysis (DTA). The phoyoluminescence studies confirms the strong intense blue emission.

Keywords: XRD, FTIR, RAMAN, crystal growth, Microhardness

1. Introduction

Enormous single crystals of good features are rare in nature. Hence many of the large single crystals for technical applications and scientific investigations are fabricated in laboratories under controlled conditions. Nowadays most of the researchers are focused on developing new high quality NLO crystal in organic and inorganic compounds due to their numerous applications [1, 2]. Most of the organic compounds have a conjugated electron system containing an electron acceptor group in the other which bring on a high NLO efficiency [3]. The inorganic materials exhibit strong absorption in the visible region and thus are not suitable for several applications but they are used in the applications of high melting point, high mechanical strength, and high degree of chemical inertness [4], and also the inorganic materials have good chemical flexibility, good thermal and mechanical stability and high tramisttance [5]. Among the inorganic materials sulphamate derivatives are better for NLO property with its two planar rings configuration and good blue light transmittance [6].

Sulphamic acid is the monoamide of sulfuric acid has an orthorhombic structure and the properties of this material have not modified for many years. It is a strong inorganic acid and shows zwitterionic form while mixing with water. Sulphamic acid finds good applications in multi stage flash evaporation (MSF) desalination plants for cleaning demisters heat exchangers cooling water systems etc [7]. Laterly in Japan the industries have established this reagent as a standard substance for titrimetric investigations , and its derivatives have vast industrial applications such as anticorrosive agent or cross linking agent for polymers [7, 8]. Some reports are available on the growth of pure and doped sulphamic acid crystals by solution and the Sanakaranarayana-Ramasamy (SR) method.[10-18].

As per the knowledge of authors and available literature there is no report available on the growth and characterization of L-proline added sulphamic acid single crystals.

2. Experimental Methods

The crystals of pure sulphamic acid and L-proline added sulphamic acid were grown by slow evaporation technique using the AR grade sulphamic acid and L-proline powders. To grow L-proline added sulphamic acid crystal the AR grade sulphamic acid and L-proline in the molar ratio 3:1 were taken and dissolved in deionized water. This mixture was stirred well using magnetic stirrer for several hours at room temperature until well liquefied. The saturated solution was filtered using a filter paper. The filtered 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 allowed to crystallization at room temperature. Good transparent and colorless crystals were collected after 20 days. Fig. 1 shows the photograph of the grown sulphamic acid (named as SA) and L-proline added sulphamic acid (named as LPSA) crystals.

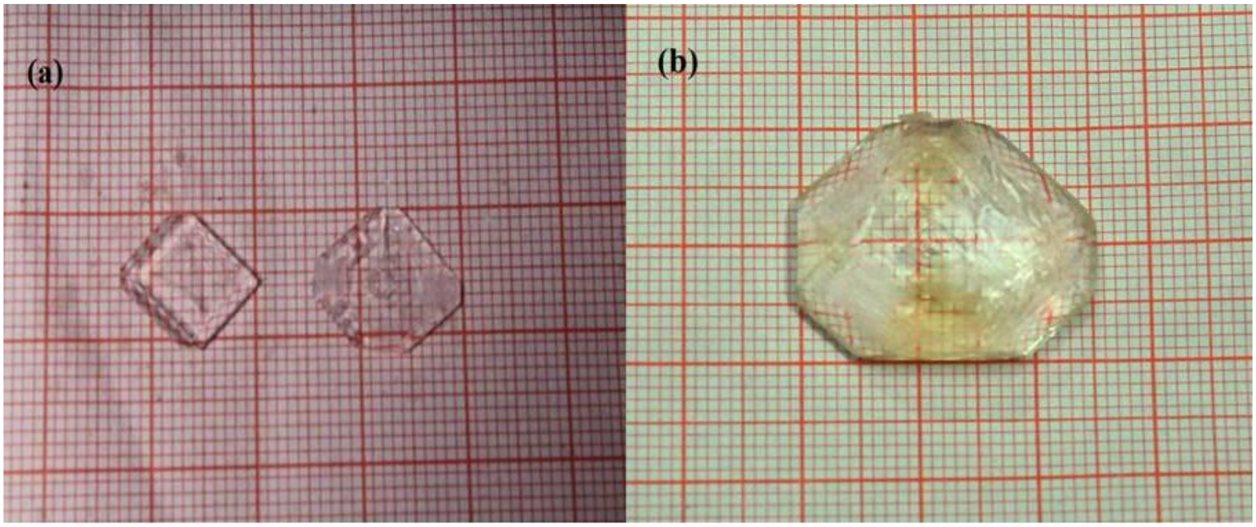

Fig.1. Photographs of the grown crystals (a) SA (b) LPSA

3. Results and discussions

3.1. Powder X-ray diffraction

The powder XRD pattern of sulphamic acid and L- proline added sulphamic acid are shown in Fig. 2. Powder X-ray diffraction (PXRD) analysis was carried out by irradiating the crystal with Cu K_{α} radiation (λ = 1.5406 Å) using PANalytical XPERT-PRO diffractometer. The sample is scanned for a 2θ range of 10°-80° . The grown SA and LPSA crystals exhibit orthorhombic crystal system. All the diffraction peaks were matched with the standard ICDD pattern (JCPDS Card No.: 70-0060). The strong intensity peak (221) was obtained for pure sulphamic acid. Therefore many grains will be oriented in the [221] direction, (021), (210) and (211) peaks belongs to orthorhombic structure was identified. Hence we know that the grown crystals were phase pure and orthorhombic structure [9]. When L- proline was added with sulphamic acid, intensity modification was observed. In LPSA crystal the observed most intense peak was (102). Comparing to pure SA crystal, in L- proline added crystal the intensity of intense peak (221) was decreased drastically. Besides the intensity of (111), (002), (021), (210), (211) and (122) were also reduced invariably. In L-poline added sulphamic acid the preferred grain orientation was along [102] plane. Here, no impurity peaks were noticed and all the peaks were fitted to the orthorhombic crystal structure, it was confirmed that L- proline added sulphamic acid also exhibits similar structure [26]. Using unit cell software package the unit cell parameters were calculated and tabulated. From the table 1, it was noticed that the unit cell parameters matches well with the standard lattice parameters of sulphamic acid. Addition of L- proline to sulphamic acid lead to shrinkage of the a-axis and elongation of b and c axis of the orthorhombic cell. Hence, the volume of the lattice has been decreased due to shrunken unit cell. This also confirmed the addition of L- proline in to the lattices of SA.

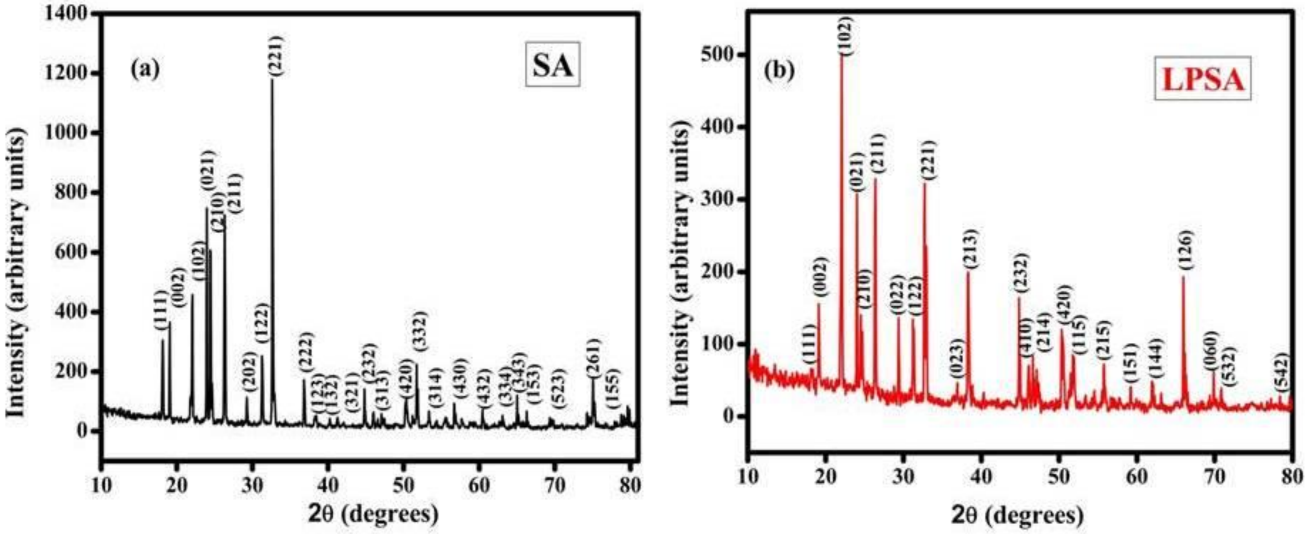

Figure 2. Power X-ray diffraction patterns of (a) SA and (b) LPSA crystals

Table 1. Structure and lattice parameters of pure SA and LPSA single crystals.

Crystal	Structure	a(A$^{\circ}$)	b(A$^{\circ}$)	c(A$^{\circ}$)	Volume (A^3)
SA	Orthorhombic	8.1266	8.0928	9.2298	607.0166
LPSA	Orthorhombic	8.0892	8.0687	9.2298	602.4233

3.2. Fourier Transform Infrared Analysis

Fig. 3 displays the recorded FTIR spectra of pure SA and LPSA crystals. The Fourier transform infrared (FTIR) spectra was recorded between 4000 to 400cm^{-1} by using Thermo Nicolet 380 FTIR spectrophotometer. The FTIR spectrum of SA showed all the characteristic functional group bondings were specified and depicted in Table 2. The IR band showed at 1002 cm^{-1} was related to the rocking mode vibration of NH_3^+ ion thus confirmed the zwitter ionic nature of sulphamic acid crystal [35]. The bands observed at frequencies around 2873 cm^{-1} and 3153 cm^{-1} respectively were owing to NH_3^+ vibrations analogues to stretching as well as degenerative stretching modes. Moreover, the bands showed at 1447 cm^{-1} and 1541 cm^{-1}

were confirmed to symmetric and degenerated modes of vibration related to NH_3^+ deformation. The bands seen at 1267 cm^{-1} and 1068 cm^{-1} were due to degenerated and symmetric SO_3^- stretching. The band appeared at 548 cm^{-1} was also assigned to degenerated SO_3^- deformation. The N-S, N-H and S-H stretching vibrations were observed at frequencies 690 cm^{-1}, 2023 cm^{-1} and 2458 cm^{-1} respectively [11, 28]. All the observed IR bands were in good agreement with earlier reports and related to theoretically calculated band frequencies. Thus from the recorded FTIR spectrum of SA it was observed that all the characteristic IR bands of functional groups along with zwitter ions were observed. Hence the grown SA crystal was phase pure and exibited orthorhombic structure. [36, 37]. However in L- proline added sulphamic acid all the peaks were seen whereas the band intensities were modified.

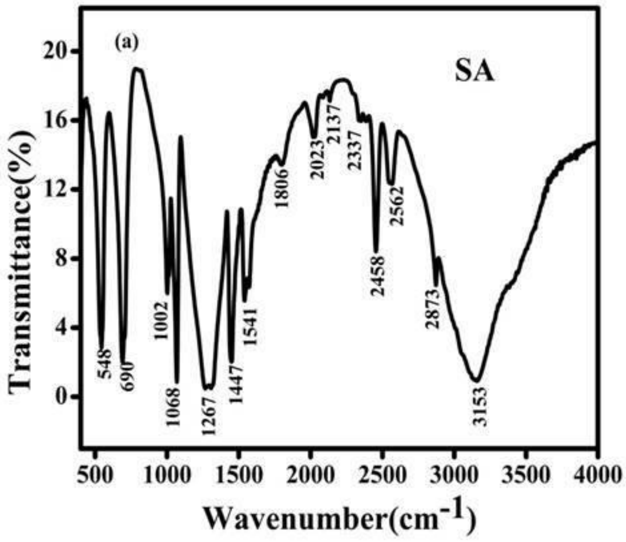

Fig 3a. FTIR spectra of pure SA crystal

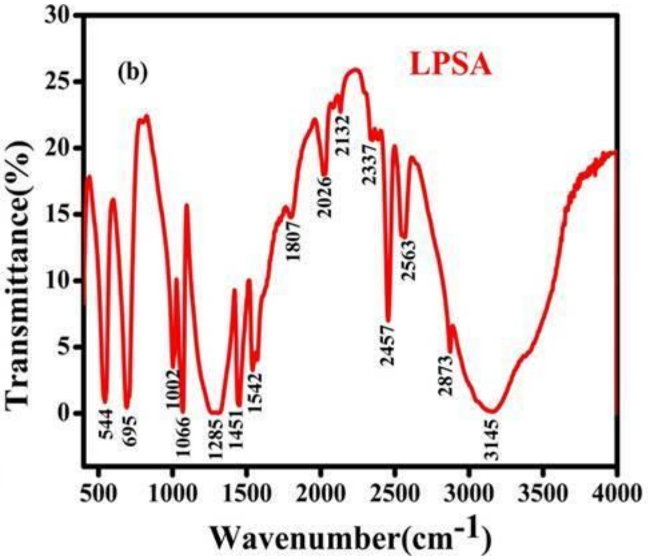

Fig 3b. FTIR spectra of LPSA crystal

3.3 Raman analysis

Raman modes were examined using imaging spectrograph STR 530mm Focal Length Laser Raman Spectrometer. The recorded Raman spectra of SA and LPSA crystals are shown in Fig. 4. The high intensity vibration band occurred in the frequency region near 1059cm^{-1} was correlated to symmetric SO_3^- stretching. The vibrations appeared at 1281 cm^{-1} and 1345 cm^{-1} were assigned to degenerate SO_3^- stretching modes. The band seen at 1017 cm^{-1} was depicted to degenerated NH_3^+ rocking vibration .The N-S stretching vibration was observed at 682 cm^{-1} . The vibration bands noticed at 543 cm^{-1} was assigned to degenerated SO_3^- deformation and vibration band observed at 363 cm^{-1} was related to the presence of SO_3^- rocking vibrations[38,39-43].From the assigned Raman modes, it was verified that SA and LPSA crystals possess orthorhombic structure. In L- proline added sulphamic acid only slight changes in peak positions were observed. The intensity of the high intense vibration band associated to degenerated SO_3^- deformation was almost retained in the same peak position. All the other peaks were slightly deviated than pure SA. Hence it was confirmed that the addition of L- proline to sulphamic acid not at all disturbed the structure of sulphamic acid, however small variations have been occur in the geometry of the structure.

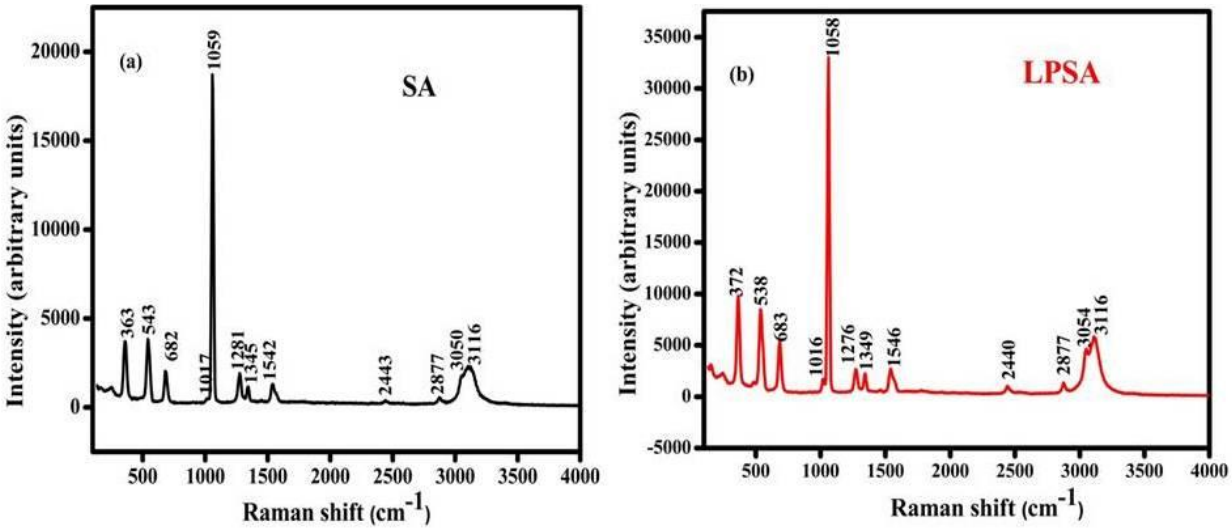

Figure 4. Raman spectra of (a) SA and (b) LPSA crystals

Table 2. Vibrational assignment of the pure and L-proline added SA single crystal

Wave number(cm^{-1})				
Raman active		IR active		Assignment
SA	LPSA	SA	LPSA	
363	372	-	-	SO_3^- rocking
543	538	548	544	Degen. SO_3^- deformation
682	683	690	695	N-S stretching
1017	1017	1002	1002	Rocking mode NH_3^+
1059	1058	1068	1066	Symmetric SO_3^- Stretching
1281	1276	1267	1285	Degen.SO_3^- stretching
-	-	1447	1451	Sym. NH_3^+ deformation
1542	1546	1541	1542	Degen. NH_3^+ deformation
-	-	2023	2026	N-H Stretching
2443	2440	2458	2457	S-H Stretching
2877	2877	2873	2873	Symmetric NH_3^+Stretching
3116	3116	3153	3145	Degen.NH_3^+ Stretching

3.4 Morphology and compositional analysis

The surface morphology of grown crystal was investigated by using Scanning Electron Microscope of VEGA3TESCAN at 228x and 347x magnification. Fig. 5 represent the SEM micrographs of SA and LPSA crystals. From the micrographs it was observed that all the crystals have been agglomerated as clusters with voids. These agglomerated crystals were in non uniform shape and size. Due to uneven distribution of temperature during synthesis process, resulted in difference in shape and size. Similar agglomerated cluster like crystals have been noticed by B. Brahmaji et al [21].

The EDAX spectrum was recorded by Bruker Nano GmbH Berl in , Germany Esprit 1.9. Fig. 5. Shows the EDAX spectra of SA and LPSA crystals. In pure SA spectra the peaks associated to sulphur(S), nitrogen(N) and oxygen(O) were observed. From this it was found that pure SA consists of only the constituent elements such as sulpher,oxygen and nitrogen. But in L- proline added sulphamic acid the peaks related to the elements S, N, O were seen. In addition the peak carbon (C) was also appeared. Hence it was understand that the added L- proline was included in to the SA lattice. The elemental composition of SA and LPSA crystals were tabulated in table 3a &3b.

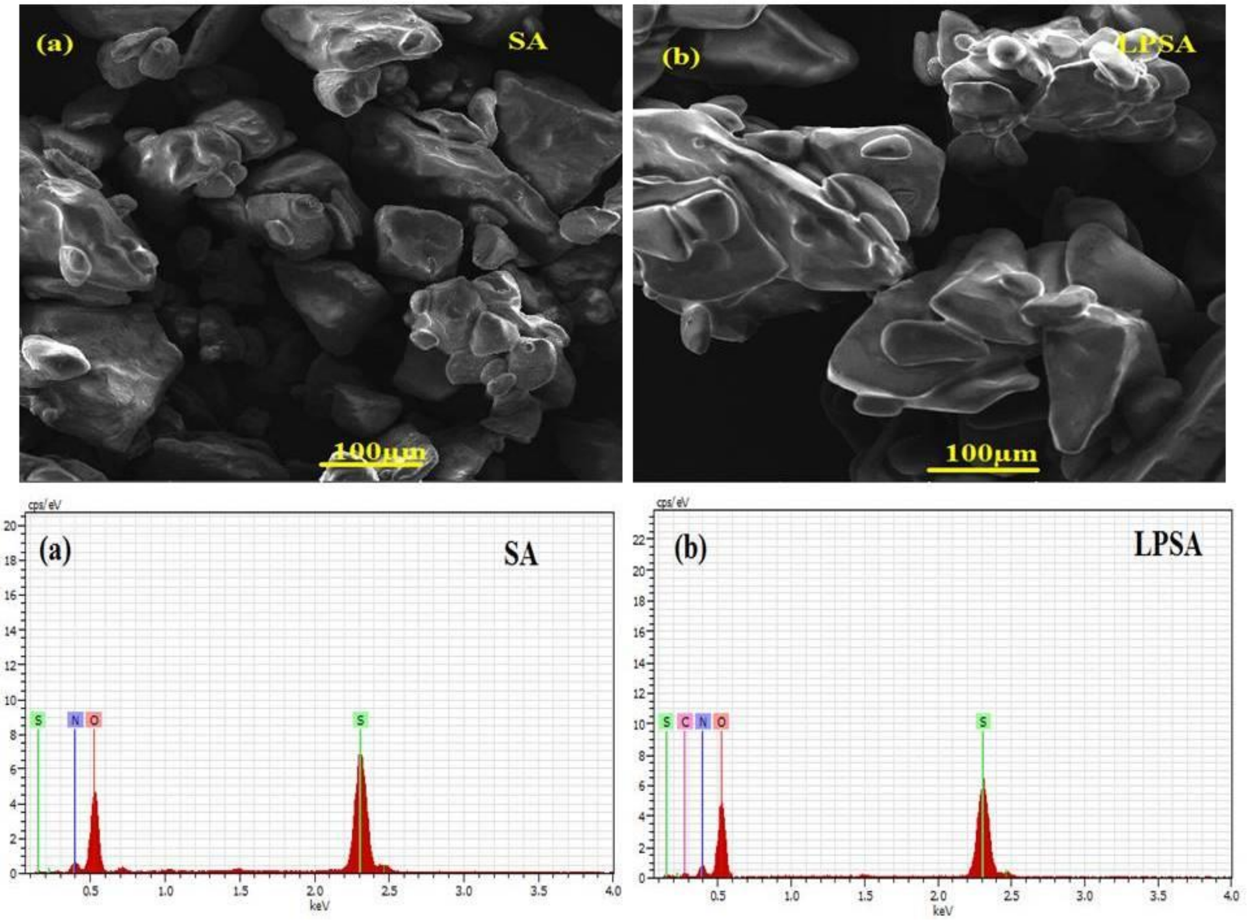

Table 3a. Elemental composition of pure SA

Element	Atomic weight (%)	Molecular weight (%)
Sulphur	12.37	22.51
Oxygen	69.71	63.26
Nitrogen	17.91	14.23

Table 3b. Elemental composition of LPSA

Element	Atomic weight (%)	Molecular weight (%)
Sulphur	19.95	34.61
Oxygen	52.48	45.42
Nitrogen	19.08	14.45
Carbon	8.48	5.51

3.5. UV-VIS studies

UV-VIS analysis of the grown crystal is carried using UV-DRS spectrophotometer in the wavelength range of 190-1100nm to find the absorbance and transmittance of the prepared crystals. The transmittance graph (Fig. 6) shows that the prepared SA and LPSA crystals have a wide range of transmission window above 360nm analogues to earlier reported results [43]. The percentage of transmittance was 86 for pure SA while for L-proline added sulphamic acid the transmittance percentage was 97. This rise in transmittance makes this material useful for photoluminescence applications. From the absorbance graph (Fig. 7) it was concluded that the lower cut-off wavelength was about 225nm for SA crystal and 242nm for LPSA crystal [44]. Inorder to find the energy bandgap of the grown crystals the graph was plotted between hν and $(\alpha h\nu)^2$ which is known as the Tauc's plot. By extrapolating the linear part of the graph (Fig. 8) to the x axis, the optical bandgap was calculated. From the graph it is found that the bandgap was 3.7ev and 3.2ev for SA and LPSA crystals respectively.

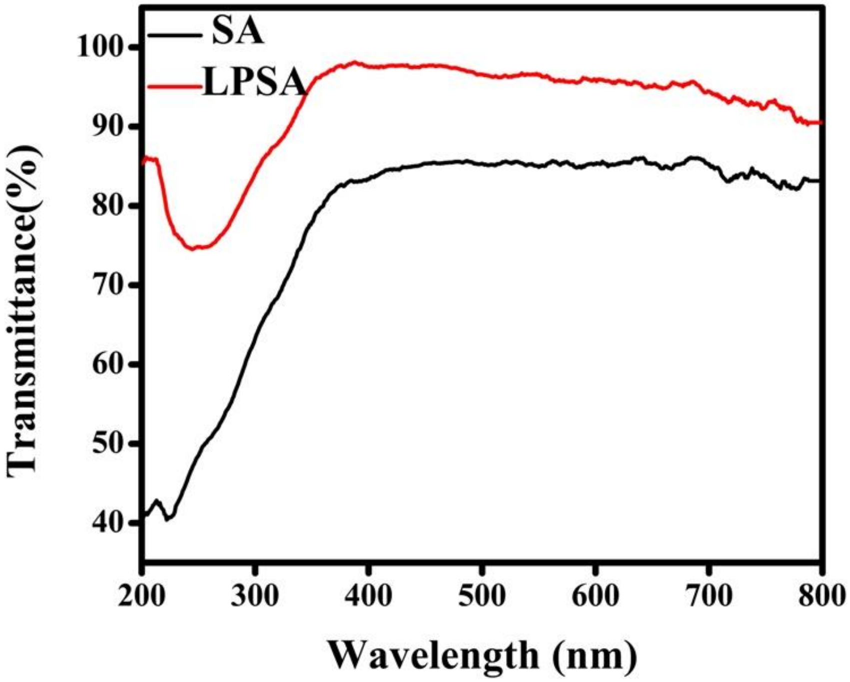

Figure 6. UV Transmission spectra of pure SA and LPSA crystal.

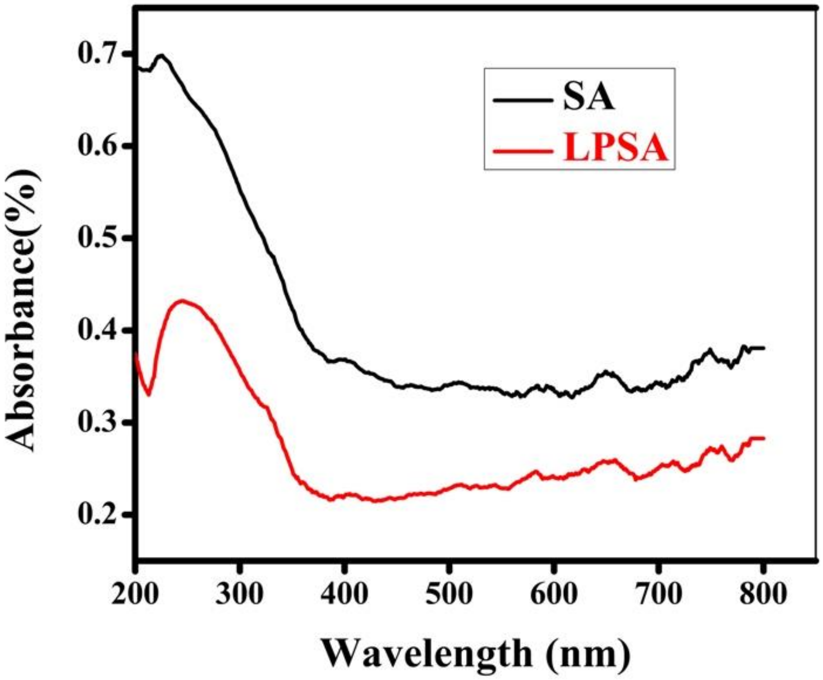

Figure 7. UV Absorption spectra of pure SA and LPSA crystal.

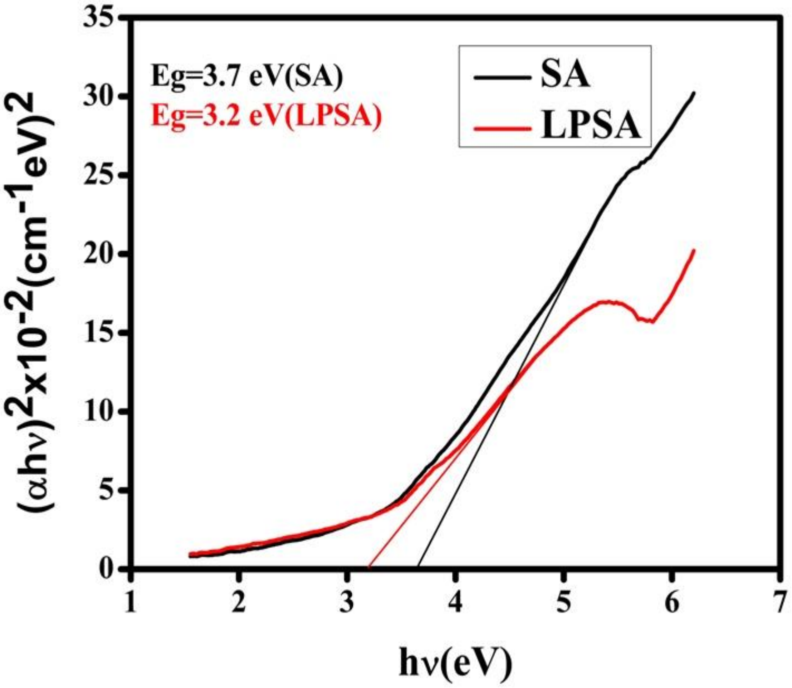

Fig.8.Tauc's plot for pure SA and LPSA crystal.

3.6. Vicker's Hardness Test :

To know the mechanical behavior of the crystals normally hardness measurement was done. The Vickers hardness of the samples was measured using the Shimadzu Model-HMV-2T. The Vickers microhardness number (H_v) can be estimated for different applied loads (p) in kg by measuring the average diagonal length of indentation (d) in mm by using the formula Hv = $1.8544P/d^2$ $kgmm^{-2}$. Fig. 9. Shows the plot of log p and hardness number. It was noted that the LPSA as earlier reports [44] was increased than SA crystals. This indicates that the purity and the quality of the SA crystal was increased by addition of L- proline. According to onitsch and Hannemann [45,29] the term hardening coefficient determines that the crystal is hard or soft. The hardening coefficient can be measured from the slope of the linear intercept plot between log p and log d. It is well- known truth that for a material if the hardness coefficient comes between 1 to 1.6 then they are called as hard crystals. For crystals whose hardness coefficient is above 1.6 are noted as soft crystals. Figure 10 shows the plot of log p versus log d. From the graph it was noticed that the hardness coefficient of both SA and LPSA crystals was above 1.6. Hence both the prepared SA and LPSA crystals can be referred as soft crystals.

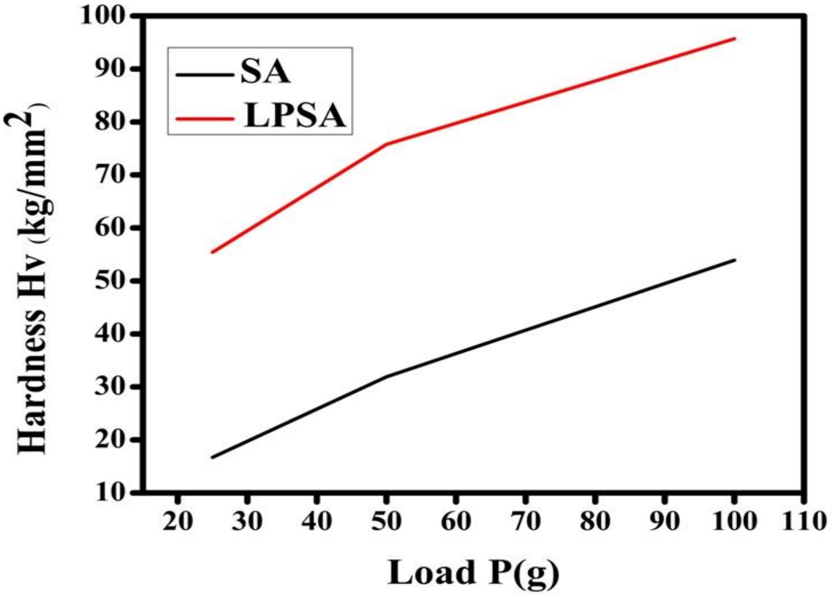

Fig.9 Plot of Load (P) Vs Hardness number(Hv) for SA and LPSA

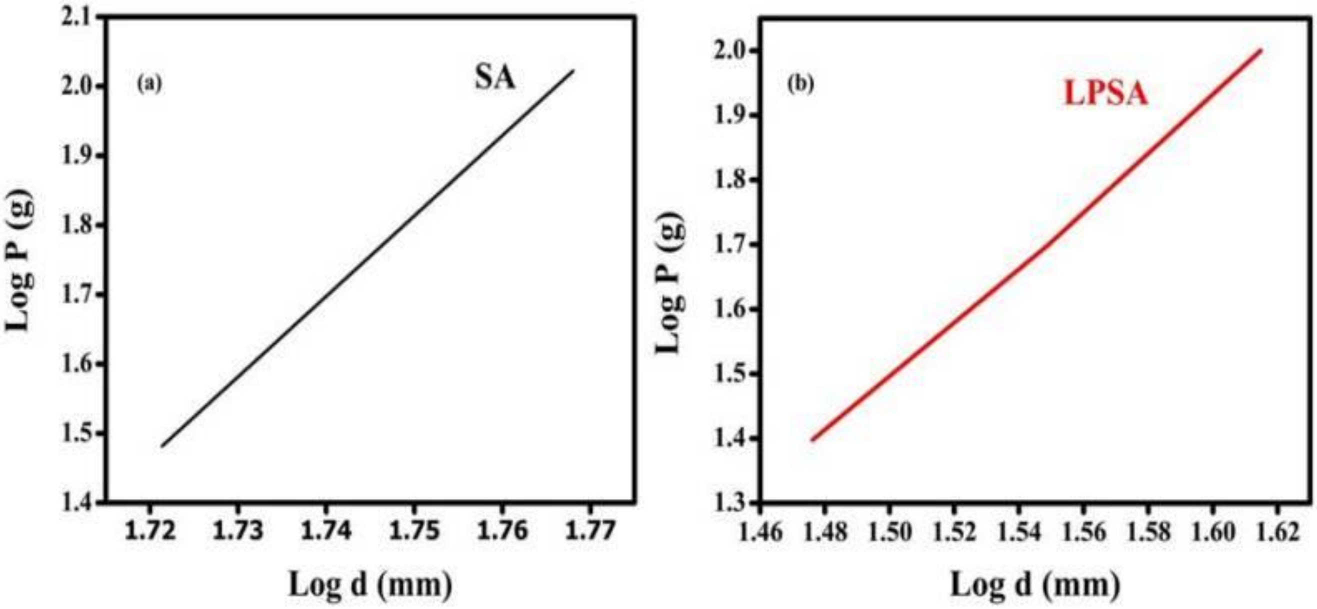

Fig 10. Log p Vs Log d for (a)SA and (b) LPSA crystal.

3.7. TG-DTA Analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were measured at a heating rate 20°c/min between 35 °C and 1000 °C in the nitrogen atmosphere using exstar/6300. Fig. 11 exhibit the TG-DTA curves of SA and LPSA crystals. It was confirmed that both crystals follows the same trend up to approximately 261 °C and no weight loss has been noticed up to this temperature. A sudden drop was appeared at 261 °C and lowers down up to 448 °C which represent the weight loss owing to the evaporation of all solvent material and water molecules. Similar peak drop was noticed in previous reports corresponding to the decomposition temperature of the crystal [21]. From DTA curves it is cleared that the endothermic peaks occurred at approximately 212 °C and 261°C in SA crystal and slightly lowered temperature LPSA crystal probably at 213°C and 258°C respectively were related to loss of water molecules and solvent elements. Similarly the sharp endothermic peak at 448 °C for SA crystal and 451 °C for LPSA crystal related to the decomposition temperature of the crystals and was compatible with TGA results. Hence the thermal stability of these crystals was good and convenient for high temperature applications below 250 ºC.

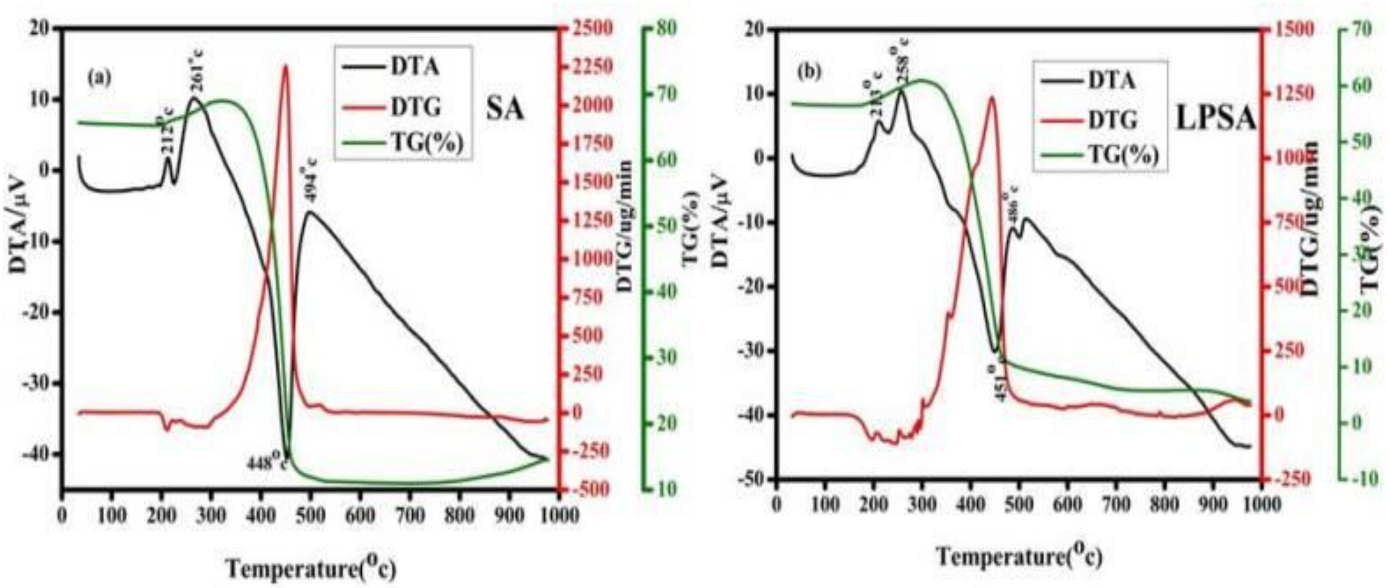

Fig.11.TGA-DTA curves of (a) SA and (b) LPSA crystal

3.8 Photoluminescence studies:

The photoluminescence of the grown crystals were studied using Varian Cary Eclipse photo luminescence spectrophotometer. The emission spectra of SA and LPSA crystals are represented in Fig.12. The emissions confirmed to ultraviolet and visible regions were noticed. The emission wavelength corresponding to violet, blue and green showed sharp peaks. The blue emission peak around 490nm-492nm has the highest intensity compared to other peaks. Normally the peaks appearing below 400nm in the UV region are corresponds to electronic transition. As expected by Arumugam et al [27] the peaks due to $\pi^- \pi^+$ emission were noticed. The peaks observed at 530nm and 542nm were related to blue and green emissions due to transition from $^5D_4$ to $^7F_6$ and $^7F_5$ energy levels respectively

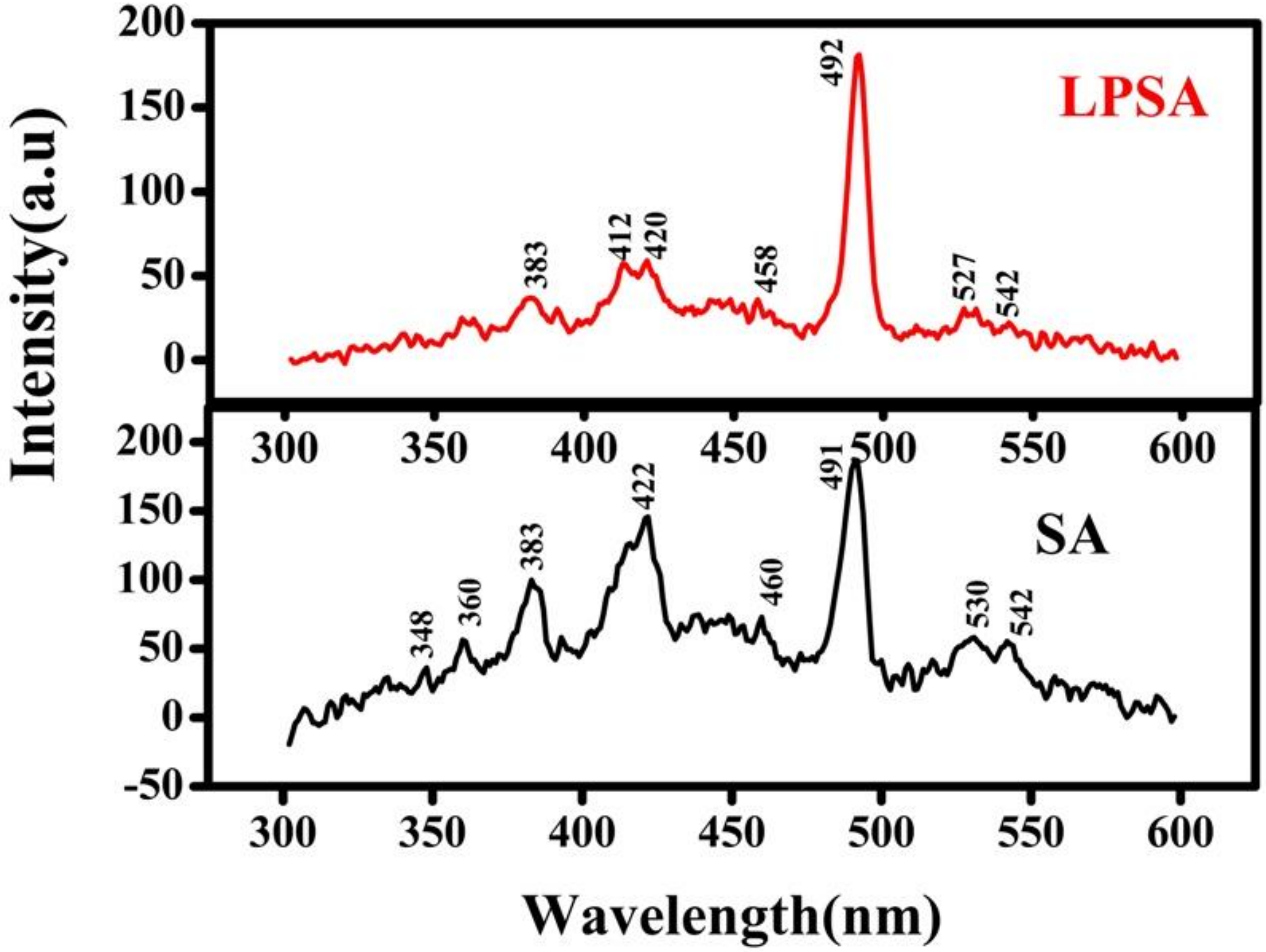

Fig.12. Photoluminescence spectra of pure SA and LPSA crystal.

IV. conclusion

The growth of pure and L-prolin added sulphamic acid crystals has been obtained by slow evaporation technique at room temperature. Powder X-ray diffraction studies confirmed the crystal structure and lattice parameters. A small variation in the lattice parameters and volume of the crystals was noticed when L-proline is added to sulphamic acid. The FTIR and FT-Raman spectroscopic analysis confirmed that there is no phase change was observed when L-proline is added to sulphamic acid and all the vibrational modes are present with small deviation in the peak position. The morphological and compositional analysis proved that, on addition of L-proline, the crystallinity was increased and the presence of carbon was noticed. The optical study shows that the crystalline perfection is goodt as the transparency is very high. The value of band gap was found to decrease between 3 and 4 with the addition of L-proline. The mechanical strength increases while adding L-proline and the crystal belongs to a soft material group. TG-DTA analysis shows that the grown crystals have thermal stability up to 261°C and 258°C. In the photoluminescence studies, the strongest peak arising from $^5D_4$ to $^7F_6$ transition at 492°C shows the blue emission. Hence this material leads to potential application in blue emission opto electronic devices.

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