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Research Article

GROWTH AND CHARACTERIZATION OF L - PHENYL ALANINE ADDED SULPHAMIC ACID SINGLE CRYSTALS

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ABSTRACT

Pure sulphamic acid (SA) and L-phenyl alanine added sulphamic acid (LPASA) were grown by slow evaporation technique. Structural analysis revealed that the orthorhombic crystal structure was retained for both the grown crystals and the crystallinity was improved upon the addition of L-phenyl alanine. The vibrational analysis of both FTIR and Raman exhibited all the vibrational frequencies related to the stretching, deformation, and zwitter ion nature of the sulphamic acid crystal. All the vibrational modes proved that the addition of L-phenyl alanine enhanced crystalline nature. The elemental analysis confirmed the presence of all constituent elements and the surface morphological study affirmed the improvement in classification of crystal grains. The transmittance was raised to 92%. Moreover, the hardness of the crystal was enhanced. The thermal stability and hardness of the SA crystal was intensified with the addition of L-phenyl alanine. The photoluminescence studies revealed that the blue emission intensity was increased on addition of L-phenyl alanine. Therefore L-phenyl alanine was considered as a good additive for sulphamic acid to improve the crystalline nature as well as the thermal and mechanical stability of the crystal. Also, the blue emission intensity was enhanced upon L-phenyl alanine addition. Hence this material may be useful for application in blue emission LED devices.

Keywords: Crystal growth, Single XRD, FTIR, Optical studies, Micro hardness, EDAX, SEM.

1. INTRODUCTION

Non - Linear Optical Materials (NLO) which shows second harmonic generation have become great importance owing to their technological improvement in optical communication, signal processing and instrumentation for the last few decades [1]. Normally, the organic NLO crystals which possess huge NLO efficiency commonly have meager thermal and mechanical characteristics and are liable to damage while processing. Also, it is difficult to grow big size optical featured crystals for device implementation. Usually, organic crystals possess high nonlinear susceptibilities in comparison with inorganic crystals. But their poor optical transparencies, laser damage thresholds, low mechanical properties restrict its use in large scale [2]. The inorganic materials are widely used for device applications because of their high melting point, mechanical strength and chemical inertness [3].

Sulphamic acid (SA) is a traditional inorganic compound and a predominant commercial chemical which was produced in kilotons [4]. It is water soluble and stable at room temperature. Due to its thermal and mechanical stability JIS (Japanese Industrial Standard), BAMC (British Analytical Methods Committee) and IUPAC (International Union of Pure and Applied Chemistry) have proposed sulphamic acid as a standard compound for titrimetric analysis. Generally, amino acids have proton donor carboxyl acid (COOH) and proton acceptor amino (NH_2) group. Usually, amino acids are widely employed in the doping of crystals because the chiral carbon atoms present in them leads the crystallization process in noncentrosymmetric space group crystals as well as retain zwitterionic nature which improves the hardness of the crystal [5-7]. However, the works on amino acid addition in non-centrosymmetric crystals are scarce. Therefore in the present work we aim to understand the hardening effect and the crystallization progress of the inorganic sulphamic acid upon addition of the amino acid L-phenyl alanine.

In this current work, L-phenyl alanine added sulphamic acid (LPASA) was synthesized as crystals by slow evaporation growing technique. The structural, morphological, optical, thermal properties, as well as hardness of the crystal, were analyzed and investigated.

2. EXPERIMENTAL

The L-phenyl alanine added sulphamic acid crystals were grown using slow evaporation method. The starting materials used were high purity sulphamic acid and L-phenyl alanine powder. Both the powders were taken in the ratio 3:1 and dissolved in double distilled water. The mixed solution was stirred using a magnetic stirrer at room temperature for several hours to get a clear transparent solution. The transparent saturated solution was filtered and transferred to the growth vessel and allowed to crystallize in a clean atmosphere at room temperature. After 20 days, good transparent colourless crystals were harvested and used for characterization purpose. The photograph of grown crystals are shown in Fig. 1.

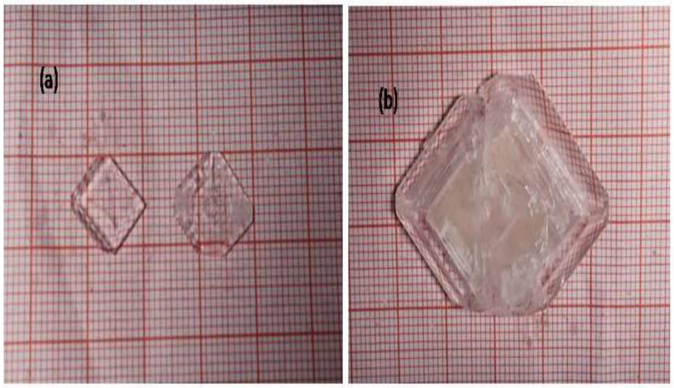

Fig. 1: Photographs of the grown crystals (a) SA (b) LPASA

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 was scanned for a 2θ range of 10°-80°. The Fourier transform infrared (FTIR) spectra were recorded between 4000 to 400cm^{-1} by using Thermo Nicolet 380 FTIR spectrophotometer. Raman modes were examined using imaging spectrograph STR 530mm Focal Length Laser Raman Spectrometer. The surface morphology of grown crystal was investigated by using Scanning Electron Microscope of VEGA3TESCAN at 228x and 347x magnification. The EDAX spectrum was recorded by Bruker Nano GmbH Berl in, Germany Esprit 1.9. UV-VIS analysis of the grown crystal is carried using UV-DRS spectrophotometer in the wavelength range of 190-1100nm. The Vickers hardness of the samples was measured using the Shimadzu Model-HMV-2T. Thermogravimetry (TG) and differential thermal analysis (DTA) were measured at a heating rate 20°C/min between 35 and 1000°C in the nitrogen atmosphere using exstar/6300. The photoluminescence of the grown crystals were studied using Varian Cary Eclipse photo luminescence spectrophotometer.

3. RESULTS AND DISCUSSIONS

3.1. Powder X-ray diffraction

Fig. 2 shows the recorded powder XRD pattern of as grown pure sulphamic acid and L-phenyl alanine 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 SA crystal the high intense peak was (221) and the other peaks also has sharp peaks. But in L-phenyl alanine added samples, the crystallinity of the sample was increased and the most intense peak was along (211) direction.

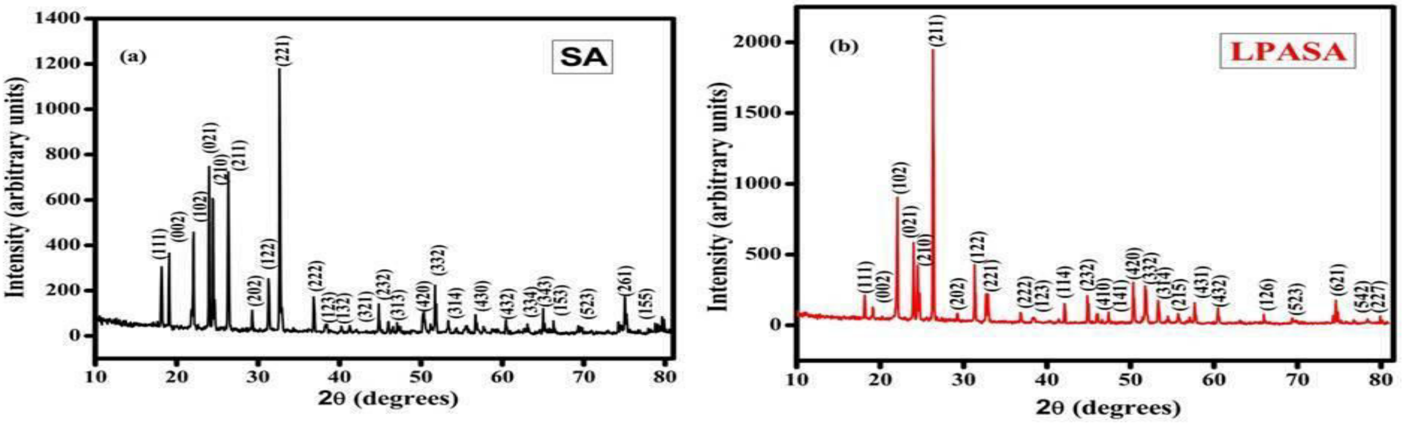

Fig. 2: Power X-ray diffraction patterns of (a) SA and (b) LPASA crystals

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

Crystal	Structure	a(A°)	b(A°)	c(A°)	Volume(A^3)
SA	Orthorhombic	8.1266	8.0928	9.2298	607.0166
LPASA	Orthorhombic	7.9649	8.1087	9.2860	599.7360

Also, the intensity of the strongest peak (211) was increased whereas the intensity of other peaks were decreased. This revealed that the addition of L-phenyl analine improved the crystalline nature of the sample and also the growth axis was enhanced along (211) direction. The change in the relative intensity of the various peaks was also noticed which proposed the successful incorporation of L-phenyl analine 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 [8-11]. From the unit cell values, it was noticed the addition of L-phenyl alanine reduces the unit cell volume even though there was elongation in b and c-axis. The reduced cell volume was due to the contraction along a-axis. This may be accounted due to grain orientation along (211) direction.

3.2. Fourier Transform Infrared Analysis

The FT-IR spectra of the grown crystals SA and LPASA are shown in fig. 3. From the spectra, it is clear that the band due to NH_3^+ mode of bonding was noticed at frequency of 3153cm^{-1} and 2873cm^{-1}. The bands observed at 2458cm^{-1} and 2023cm^{-1} were due to tribands overtones/ combinations of hydrogen bonded OH bending modes. The bands seen at 1806cm^{-1} and 1447cm^{-1} were due to deformation of NH_3^+ mode of vibration. The vibration bands observed at 1267cm^{-1} was due to degenerated SO_3^- stretching, whereas at 1068cm^{-1} was due to symmetric SO_3^- stretching. The rocking mode vibration NH_3^+ was noticed at 1002cm^{-1} which verified the formation of zwitterions in SA and LPASA crystals [12]. The N-S stretching vibration was observed at 690cm^{-1} and the band that occurred at 548cm^{-1} was due to degenerated SO_3^- deformation [13]. All the IR bands that observed in the grown crystals were in good agreement with earlier reports and were comparable with theoretically calculated bands [12, 14]. Table 2 shows the vibrational assignment of SA and LPASA crystals. However in L-phenyl alanine 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 sublattice.

Table 2: Vibrational assignment of the pure and L-Phenyl analine added SA single crystal

Wave number(cm^{-1})		Assignment
Pure SA	**LPASA**	
548	544	Degen. SO_3^- deformation
690	695	N-S stretching
1002	1002	Rocking mode NH_3^+
1068	1066	Symmetric SO_3^- stretching
1267	1255	Degen. SO_3^- stretching
1447	1444	Sym. NH_3^+ deformation
1541	1542	Degen. NH_3^+ deformation
1806	1807	Symmetric NH_3^+ deformation
2023	2026	N-H Stretching
2458	2457	S-H Stretching
2873	2873	Symmetric NH_3^+Stretching
3153	3139	Degen.NH_3^+ Stretching

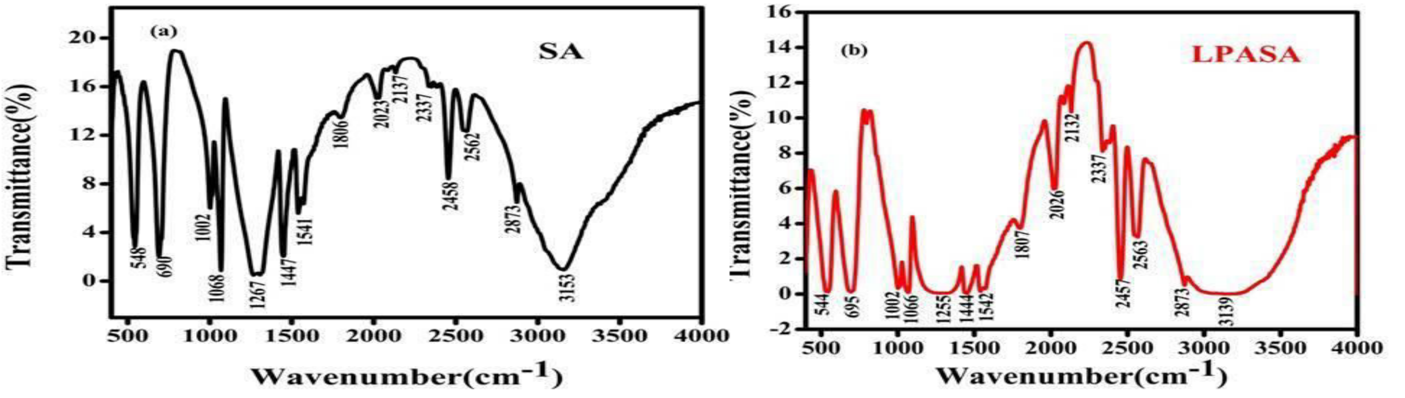

Fig. 3: FTIR spectra of (a) SA and (b) LPASA crystals

3.3. Raman analysis

The additional verification of vibrational modes was achieved by FT-Raman analysis. The Raman spectra of SA and LPASA crystals are shown in Fig. 4. Strong peak at 1059 cm^{-1} because of symmetric SO_3^- stretching vibration which was also seen at FTIR spectra. It exhibited in both spectra, since these vibrations were both IR and Raman active. The bands noticed at the peak positions 363cm^{-1}, 256cm^{-1} were due to the presence of SO_3^- rocking and N-S torsion vibrations respectively. The vibration bands observed in pure SA at 543cm^{-1} and 536cm^{-1} in LPASA were allocated to degenerated SO_3^- deformation. The band occurred at 682 cm^{-1} in pure SA and at 692 cm^{-1} for LPASA was due to N-S stretching vibration. The band arised at 1017 cm^{-1} represented NH_3^+ rocking vibration in pure SA, while that band in L-phenyl alanine added sulphamic acid was at 1014 cm^{-1}. The degenerated SO_3^- stretching vibration was observed at 1345 cm^{-1} and 1281 cm^{-1}, whereas in LPASA it was appeared at 1345cm^{-1} and 1272cm^{-1} respectively. The peak at 1542 cm^{-1} was related to NH_3^+ deformation, while that band in L-Phenyl alanine added sulphamic acid was observed at 1553 cm^{-1}. The band at 2443cm^{-1} in pure SA and 2447cm^{-1} in LPASA was due to S-H stretching vibration. The band seen at 2877cm^{-1} was associated to symmetric NH_3^+ stretching vibration in pure SA and 2884cm^{-1} for L-phenyl alanine added sulphamic acid. The vibration bands noticed in pure SA at 3116cm^{-1} and 3123cm^{-1} in LPASA were assigned to degenerated NH_3^+ stretching vibration. Since all the vibrational related to orthorhombic crystal structure of sulphamic acid was found in both spectra it was concluded that both the grown crystals possessed the similar crystal system [1, 15-20]. In L-phenyl alanine added crystals only shifted towards higher wave number was noticed. Also it was found that the intensity of the 1059cm^{-1} peak which was related to symmetric SO_3^- stretching vibration was increased on adding which confirmed the change in the geometry of the lattice even though the same orthorhombic structure was retained.

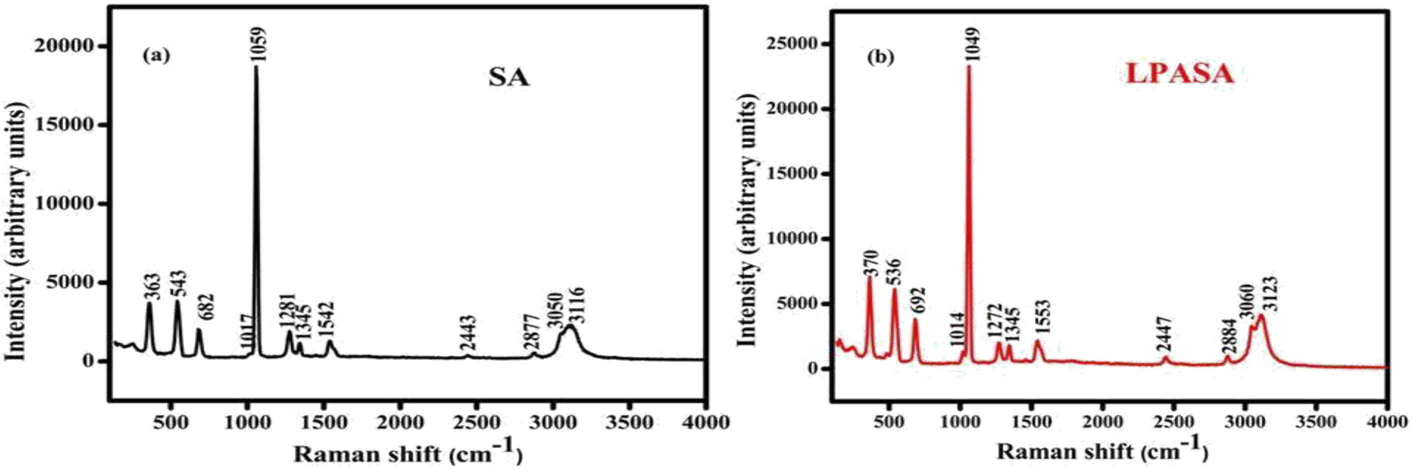

Fig. 4: Raman spectra of (a) SA and (b) LPASA crystals

3.4. Morphology and compositional analysis

The surface morphology of as grown sulphamic acid and L-phenyl alanine added sulphamic acid crystals were examined using scanning electron microscope and are shown in fig. 5. The SEM images revealed that the particles were in non uniform size and displayed agglomeration along with voids. On clear examination, it was noticed that in L-phenyl alanine 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 grown crystal was derived from the micro analytical technique known as energy dispersive X-ray analysis. Fig.5. shows the EDAX spectra of SA and LPASA crystals. The existence of various elements like oxygen, nitrogen and sulphur has been verified in sulphamic acid crystal and the presence of oxygen, nitrogen, sulphur and carbon has been confirmed in L-phenyl alanine added sulphamic acid crystal. The elemental analysis of N, S, O and carbon in the sample proposed that the incorporation of L-phenyl alanine in sulphamic acid crystals. From EDAX results the successful addition of L-phenyl alanine in to SA crystals was confirmed. The elemental compositions were tabulated in table 3a and 3b respectively.

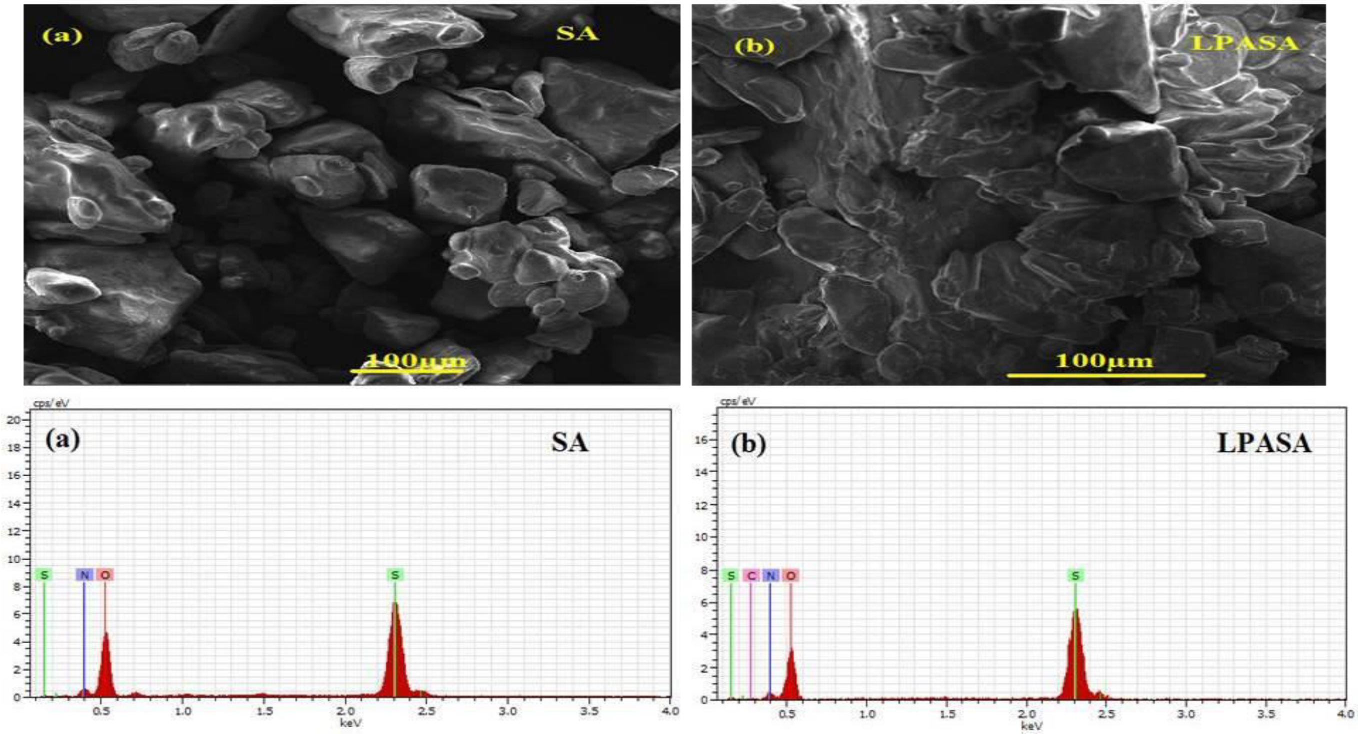

Fig. 5: SEM and EDAX analysis of (a) SA and (b) LPASA crystals

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 LPASA

Element	Atomic weight (%)	Molecular weight (%)
Sulphur	13.58	24.56
Oxygen	65.87	59.47
Nitrogen	18.05	14.27
Carbon	2.50	1.69

3.5. 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 is shown in fig. 6. It is clear from the figure that the grown crystals have transparency of 86% and 92% for pure SA and LPASA crystals respectively. The transparency of the LPASA 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 [21]. From fig. 7, it was found that the lower UV-cut off wavelength for the SA crystal was 227nm, while in LPASA it was 234nm and percentage of absorption is high for L-Phenyl a alanine added sulphamic acid in comparison with pure sulphamic acid and it could be due to the influence of L-Phenyl alanine [22]. The tauc's plot analysis was carried out to find the energy band gap values and shown in fig. 8. The obtained optical band gap energies of pure and L-Phenyl alanine added sulphamic acid were 3.7eV and 3.0eV respectively.

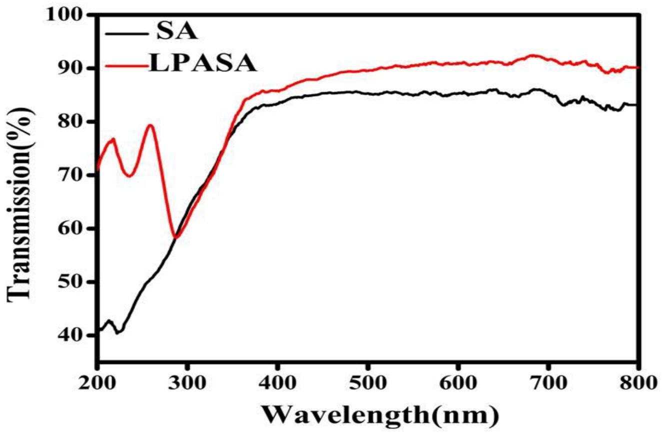

Fig. 6: UV Transmission spectra of pure SA and LPASA crystal

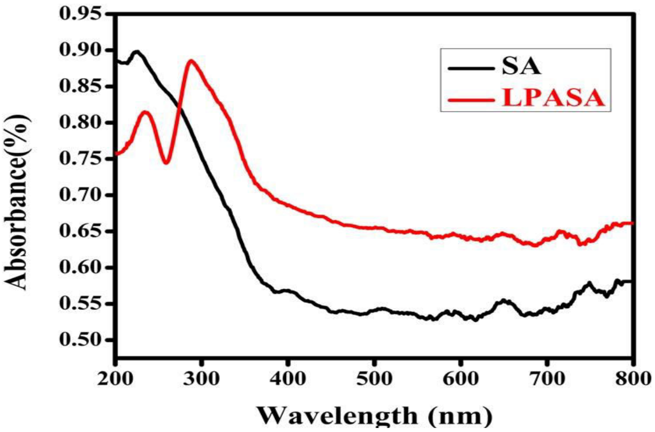

Fig. 7: UV Absorption spectra of pure SA and LPASA crystal

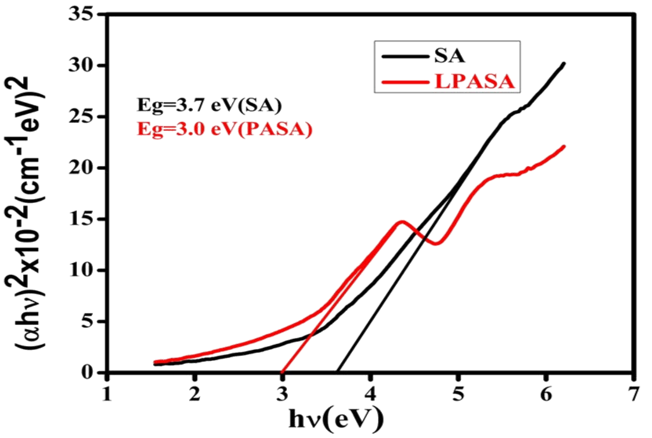

Fig. 8: Tauc's plot for pure SA and LPASA crystal

3.6. Vicker's Hardness Test

The applications of the crystals are dependent on optical performance as well as good mechanical behavior [23, 24]. Vickers micro hardness measurements were done for the SA and LPASA crystals at room temperature with the load ranging from 25g to 100g. The diagonal lengths of the indentation (d) were calculated in μm for various applied loads (p) in g. Vickers hardness number was determined from the following relation

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

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, there is no crack has been observed. The presence of L-Phenyl alanine played a important role in increasing the hardness property of the SA crystal. Similar behavior has been reported by Arumugam et al and Babu et al. [7, 9]. The work hardening coefficient was studied from the plot of logp versus logd, and the results are shown in Fig. 10, Least square fitting gives straight line graph, which are in good accordance with Meyer's law. The value of n is calculated from the slope of the graph. According to Hanneman and onitsch [25] n should lie between 1 and 1.6 for hard materials and above 1.6 for soft materials. Thus LPASA and SA crystal belong to soft material group.

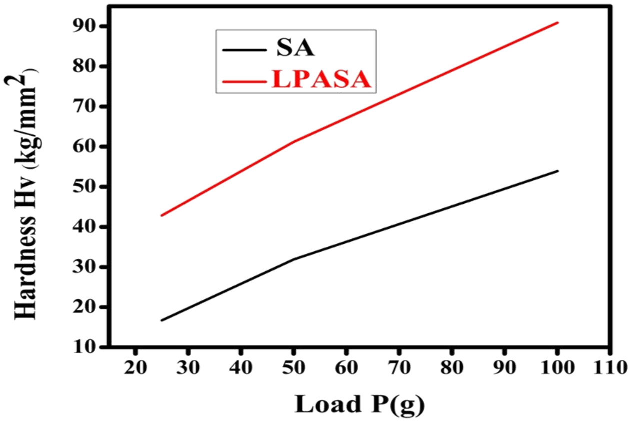

Fig. 9: Plot of Load (P) Vs Hardness number (Hv) for SA and LPASA

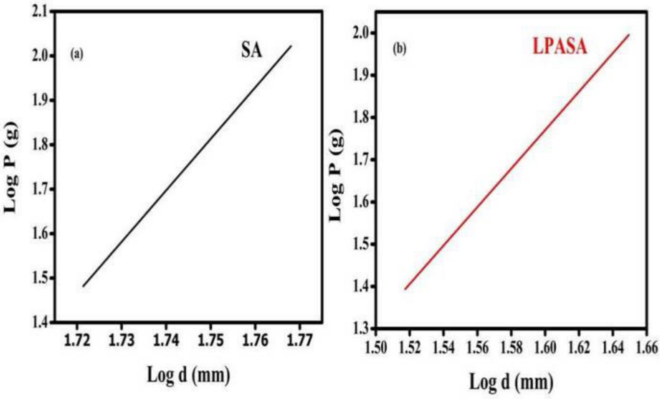

Fig. 10: Log p Vs Log d for (a) SA and (b) LPASA crystal

3.7. 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 [2]. TGA/ DTA analysis of pure SA and L-Phenyl alanine in added SA is shown in Fig. 11. It is noticed that there is no weight loss of the samples up to 212°C to 261°C. There was a sudden weight loss from 261°C to 448°C. Total weight loss can be observed at 449°C onwards. The nature of weight loss indicate the decomposition point of the material. Total decomposition of the crystal takes place at temperature 448°C for SA and 450°C for LPASA crystal. Hence these compounds have good thermal stability upto 212°C and 203°C for pure SA and LPASA crystals. Hence we can say that the grown crystals are suitable for applications with working temperature up to 212°C and 203°C.

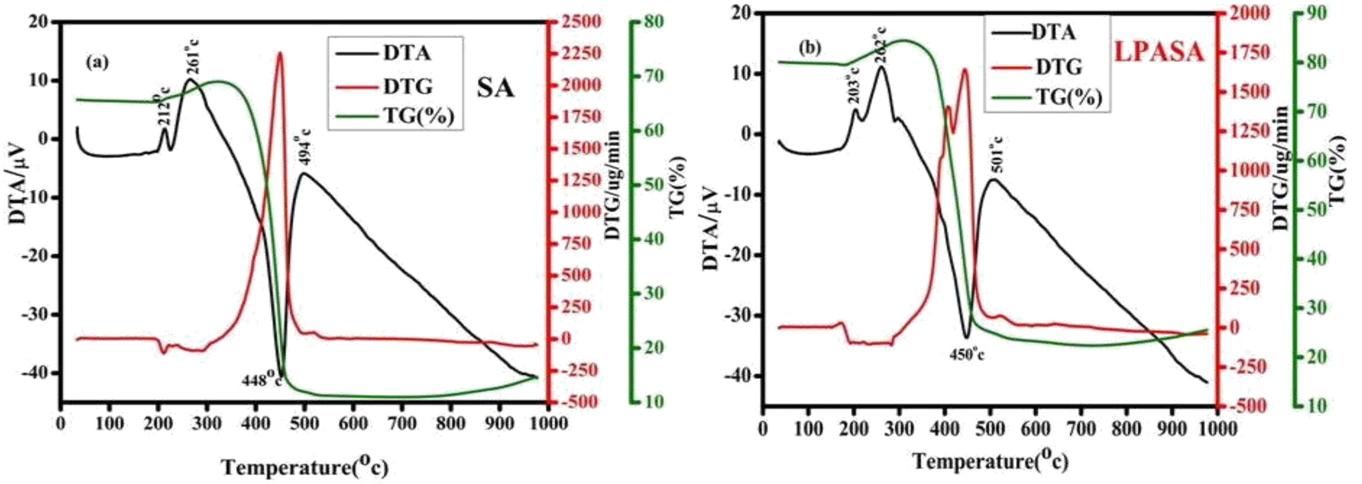

Fig. 11: TGA-DTA curves of (a) SA and (b) LPASA crystal

3.8. Photoluminescence studies

The emission spectra of SA and LPASA crystals are shown in fig 12. The emission spectra shows the emission in the ultraviolet and visible regions.

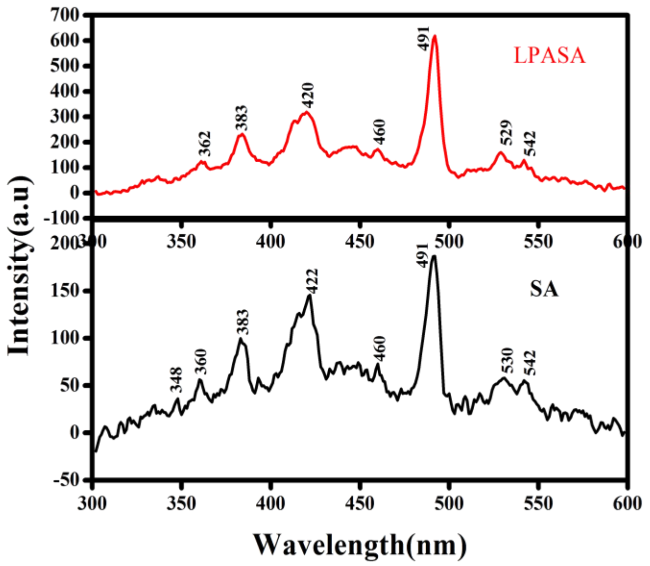

Fig. 12: Photoluminescence spectra of pure SA and LPASA crystal.

The violet, blue and green emissions were observed in the visible region. Amid all the emissions that observed, the strongest emission was occurred at 491 nm analogues to blue emission. The peaks observed below 400 nm observed in the ultra violet region were owing to electronic transition $\pi^{-}\pi^{+}$ as reported by Arumugam et al. [7]. The peaks noticed below 500 nm were corresponding to blue emission [26]. Due to transition between the energy levels $^5D_4$ to $^7F_6$, these emissions were happened. The peak observed at 530 was linked to green emission due to transition from $^5D_4$ to $^7F_5$ energy levels [27]. On close examination, it was found that the intensity of blue emission was enhanced. The property of having strong emission in blue region may lead to potential application of this material in blue emission optoelectronic devices [28].

4. CONCLUSION

The growth of pure and L-phenyl alanine added sulphamic acid crystals have been attained by slow evaporation technique at room temperature. Powder X-ray diffraction studies verify the crystal structure and lattice parameters. A small change in the lattice parameters and volume of the crystals was noticed when L-phenyl alanine is added to sulphamic acid. The FTIR and FT-Raman spectroscopic analysis verified that there was no phase change noticed when L-phenyl alanine was added to sulphamic acid and all the vibrational modes were present with slight deviation in the peak position. The morphological and compositional analysis proved that, on addition of L-phenyl alanine, the crystallinity was improved and the presence of carbon was identified. The optical study shows that the crystalline perfection is excellent as the transparency is very high.

The value of band gap was found to decrease between 3 and 4 with the addition of L-phenyl alanine. The mechanical strength rises while adding L-phenyl alanine and the crystal goes to a soft material group. TG-DTA analysis shows that the grown crystals have good thermal stability up to 212°C and 203°C. In the photoluminescence studies, the strongest peak arising from $^5D_4$ to $^7F_6$ transition at 491°C shows the blue emission. Hence, this material leads to potential application in blue emission opto electronic devices.

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Conflict of interest

None declared

6. REFERENCES

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