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Influence of ammonium sulphate on L-alanine single crystals (LAAS) for NLO applications

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Abstract: *NLO materials have a nonlinear response to the electric field of the light of a laser beam. Most of the amino acids are NLO materials that find application in field of optical communication, information technology, signal processing and industrial applications. The NLO active material such as L-alanine is mixed with ammonium sulphate to form novel NLO material for the first time. Ammonium sulphate admixtured L-alanine crystals (LAAS) were grown successfully by solution method with slow evaporation technique at room temperature. The grown crystals were colorless and transparent. The solubility of the grown samples has been found out at various temperatures. The lattice parameters and structure of the grown crystals were determined by X-ray diffraction technique. UV–visible transmittance spectrum was recorded to study the optical transparency of grown crystal. The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz–Perry powder technique. Hardness measurement was also carried out to measure the mechanical stability of the grown crystal. EDAX spectrum has been taken for elemental analysis. TG/DTA measurements were also obtained to know the thermal behavior of the sample.*
Keywords*: Crystal growth; NLO; SHG; microhardness; Thermal;*

I. Introduction

The search and design of highly efficient nonlinear optical (NLO) crystals are extremely important for optoelectronics processing. The development of NLO materials led to compounds potentially suitable for application in frequency conversion, optical telecommunication, image processing, optical computing and data storage devices. Amino acid crystals have been subjected to extensive investigation by the researchers for their nonlinear optical properties for the past years. Among the amino acids, L-alanine is the simplest molecule with second harmonic generation efficiency of about one-third of that of the well known KDP. If L-alanine is mixed with different inorganic acids and salts to form novel materials, it is expected to get improved NLO properties [1-2]. Some complexes of L-alanine have been recently crystallized and various studies have been investigated by many researchers [3-4]. Adding some inorganic materials with NLO materials will help us to get crystals with enhanced physical and chemical properties [5]. So first time we report here the Ammonium sulphate admixtured L-alanine crystals for optoelectronics application. The grown crystals were subjected to various characterization techniques like single crystal XRD, Optical transmission, EDAX, second harmonic generation, thermal analysis and mechanical analysis. The results of these analyses are discussed in this paper.

II. Synthesis, Solubility And Growth

Ammonium sulphate admixtured L-alanine (LAAS) salt was synthesized by dissolving high purity L-alanine and ammonium sulphate $(NH_4)_2SO_4$) in the ratio of 2:1 in double distilled water. Solubility study was performed for different temperatures using by gravimetrical method [6]. From the figure 1, it is observed that the solubility of LA and LAAS sample in water increases linearly with temperature, exhibiting a high solubility gradient and positive temperature coefficient, which reveals the fact that slow evaporation technique is the appropriate method to grow single crystals of LA and LAAS. And the solubility values of LAAS are increased than pure LA due to the changes in thermodynamic parameters. In accordance with the solubility data, saturated solution of the twice re-crystallized salt of LAAS and LA was prepared and allowed for slow evaporation technique for growth process. It is observed from the figure 2 that the morphology and size of L-alanine crystal seem to be different when it was grown in aqueous solutions of ammonium sulphate due to the entry of admixtured chemical into the lattice of L-alanine crystals. [7].

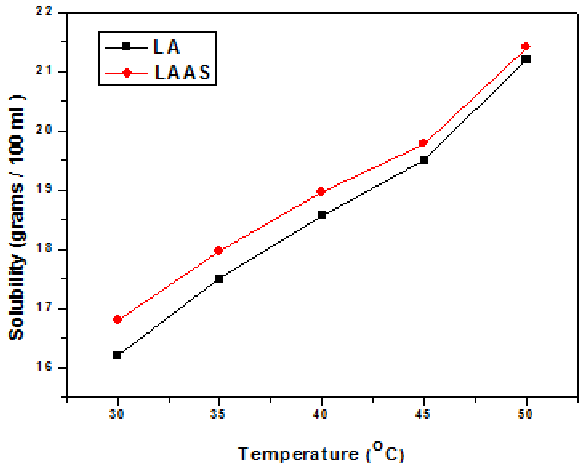
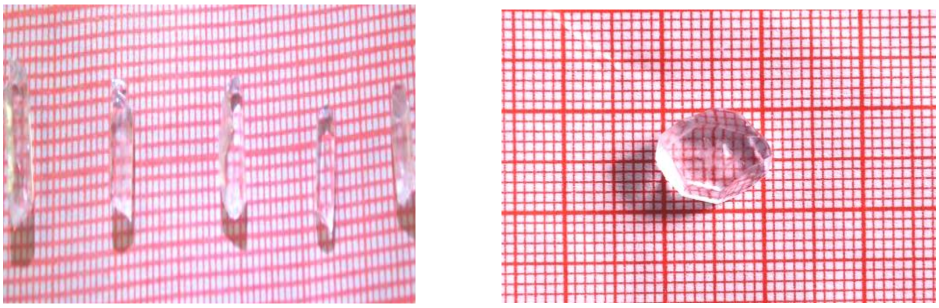


Figure 1: Solubility curve for grown samples



(a) (b)

Figure.2: Grown crystal of (a) pure L-alanine and (b) Ammonium sulphate admixtured L-alanine (LAAS)

III. Results And Discussions

3.1 Single Crystal XRD Analysis

The obtained lattice parameters of LAAS sample from a single crystal X-ray diffraction are a=5.769(14)Å, b=6.031(17)Å, c=12.342(6)Å, α=β=γ=90° and V = 429.41(11) $Å^3$ which are almost coincided with those of L-alanine crystal [8]. The grown samples are crystallizes in orthorhombic crystal system with non-centro symmetric space group $P2_12_12_1$.Slight changes in lattice parameters may be due to incorporation of admixtured material.

3.2 Second Harmonic Generation Analysis (SHG)

The second harmonic generation (SHG) efficiency of the grown samples was determined by Kurtz and Perry [9].A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered sample. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ = 532 nm). The SHG efficiency of the grown LA and LAAS crystals was found to be 0.33 and 0.74 times than that of KDP respectively. So Comparing L-alanine the LAAS sample has enhanced SHG efficiency for optoelectronics application.

3.3 Chemical Composition Analysis

The EDAX spectrum of the LAAS sample was taken for elemental analysis. From the figure 3, it is confirmed that the elements such as carbon, oxygen, nitrogen and sulphure are present in the sample. To confirm the presence of hydrogen, CHN analysis was also carried out and it is found that percentage of hydrogen present in the sample is 8.73 wt%.

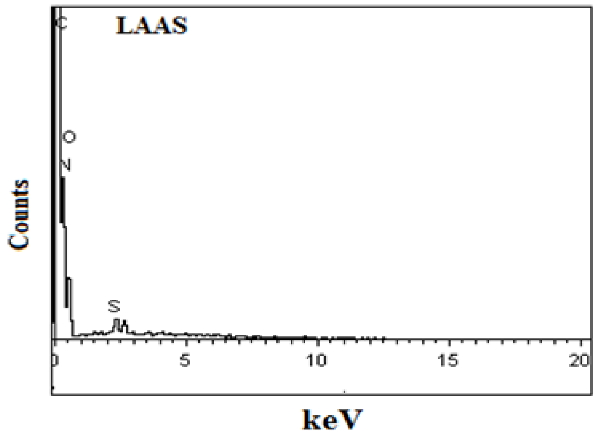


Figure 3: EDAX spectrum of LAAS sample

3.4 Optical Transmission Spectral Analysis

The optical transmission spectra of the grown crystals were recorded by UV-vis spectrophotometer in the range 190nm – 1100nm. The crystals are found to have good transmittance (Figure 4) in the visible region and it is noted that the UV transparency cut-off occurs at 242 nm and 235 nm respectively. The good transparency and lower cut-off wavelength of these materials enable them to be a good candidate for optoelectronic applications [10]. The band gap value of LA and LAAS sample is found to be 5.12 eV, 5.28 eV respectively. The high transmittance in the visible region and high band gap is an encouraging optical property seen in the spectra of the grown crystals and is of vital importance for NLO applications. It is also noticed that the transmittance percentage of LAAS crystal is enhanced than the transmittance percentage of L-alanine. This enhancement has been attributed to the enhancement in crystalline perfection with reduction of the vacancies. Slight shifting in lower cut-off wavelength may be due to the low and moderate incorporation of ammonium sulphate in the L-alanine crystals.

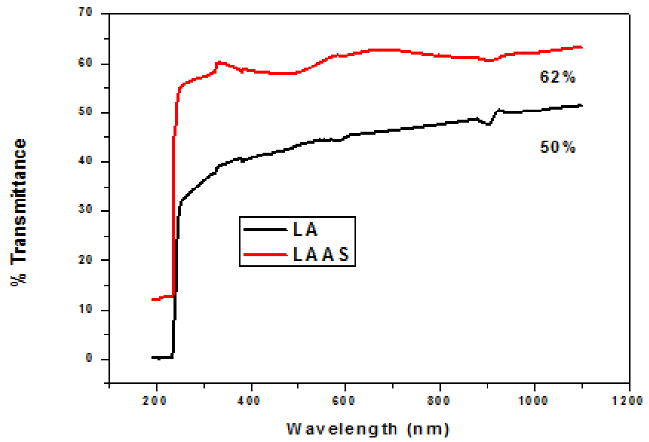


Figure 4: Optical transmission spectra of grown samples

3.5 Mechanical Analysis

Microhardness testing is one of the best method to understand the mechanical properties of materials. It was carried out using Vickers microhardness tester for grown samples. The hardness number was calculated using the relation $H_v = 1.8544\ P/d^2$ where P is applied load and d is diagonal length of indentation impression. It is observed from the figure 5 that the hardness number of grown samples increases with the increase of load and obeying the reverse indentation size effect. The plot log (P) verses log (d) is drawn to find work hardening coefficient (n) for the samples. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials[11]. Hence, it is concluded that LAAS and LA crystals are soft material as they have 'n' value more than 1.6 (table 1). Hardness of LAAS is higher than that of LA crystals which may be due to the incorporation of impurities in the lattice of L-alanine crystals. The presence of impurities may reduce the weak lattice stresses on the surface of the grown crystals and hence the LAAS crystals became harder than the pure L-alanine crystal. This indicates that greater stress is required to form dislocations thus confirming greater crystalline perfection. This is the favorable result for device fabrication to withstand during high laser intensities.

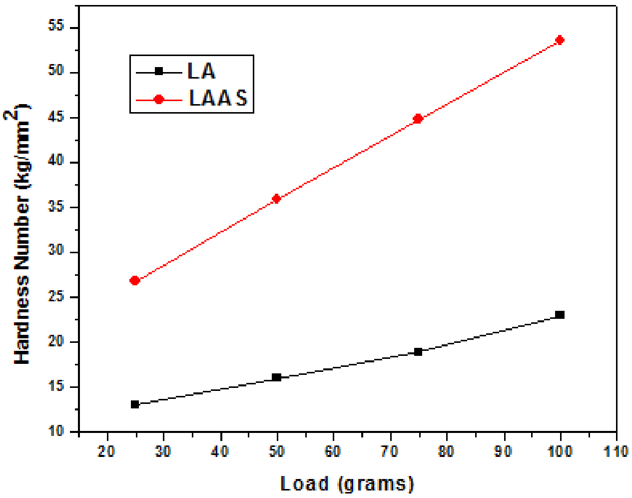


Figure 5: Dependence of Hardness with load of grown crystals

The yield strength and stiffness constant of grown samples were calculated using the relations (σ_y) = (H_v/3) $(0.1)^{n-2}$ and $C_{11} = H_v^{7/4}$ respectively. The values are depicted in table 1.It is observed that the values of yield strength of the grown crystals are increase with the applied load and hence the grown crystals have relatively high mechanical strength. And the stiffness constant increases with increase of load for the crystals. High values of C_{11} for the grown crystals indicate that the binding forces between the ions are quite strong [12].

Table 1: Hardness parameter values of LA and LAAS single crystals

Sample	Load (g)	Hardness Number (kg/mm^2)	Yield strength X 10^6 pascal	Stiffness constant X 10^{14} pascal	Work hardening coefficient number (n)
LA	25	13.04	1.20	1.54	3.468
	50	16.02	1.78	2.20	
	75	18.96	2.01	2.96	
	100	22.95	2.32	4.13	
LAAS	25	26.85	0.98	5.44	3.955
	50	35.95	1.32	9.06	
	75	44.82	1.64	13.33	
	100	53.60	1.96	18.24	

3.6 Thermal Analysis

The thermal studies were carried out for the samples to find out the weight change (TG), energy change (DTA) and various endothermic and exothermic transitions in the samples with the change of temperature. The TG/DTA curves of LAAS sample are presented in figure 6. The initial mass of the material was taken to be 9.327 mg and the final mass left out after the experiment was only 0.008 mg of initial mass. There is a major weight loss between 224.00 ^{o}C to 305.04^{o}C which was assigned to decomposition of LAAS. And the crystal decomposed only at 301.27°C. The sharp endothermic peak shows the good degree of crystallinity of the sample [13]. Decomposition point of LA is 250^{o}C and hence LAAS with stand to better thermal point than the LA sample.

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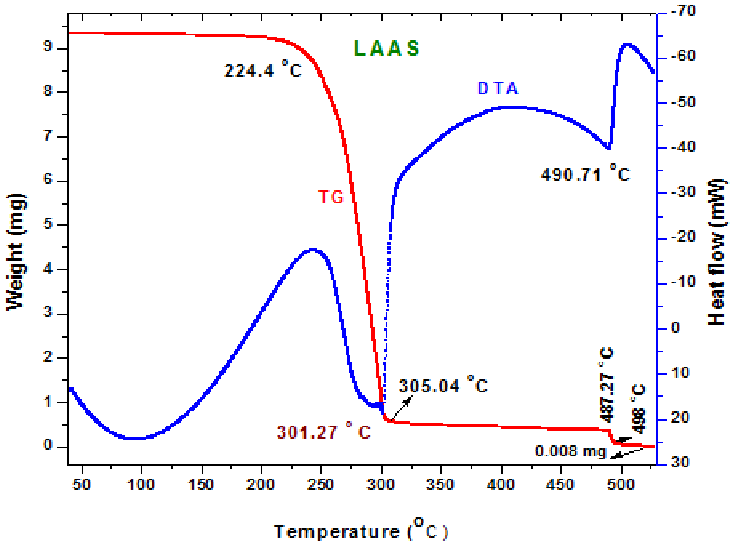

Figure 6: TG/DTA Curves for LAAS sample

3.7 Conclusion

Good quality single crystal of LAAS has been grown by slow evaporation technique. The solubility of LAAs sample was estimated for water solvent at different temperatures. The X-ray diffraction studies confirm the orthorhombic structure of the grown crystal with non-centrosymmetric space group. The optical studies reveal that LAAS crystal possesses 62% transmittance. EDAX spectrum shows the presence of elements in LAAS sample. SHG studies reveal that LAAS material is a promising material for NLO applications. Vickers microhardness value was calculated in order to understand the mechanical stability of the grown crystals. Thermal stability and decomposition point were found by TG/DTA analysis. The above results reveal the desirable property of the crystal for NLO device applications. The above studies indicate that the grown materials are good candidate for optoelectronic applications. Enhancement in the above properties of LAAS sample shows that the ammonium sulphate plays vital role in the lattice of pure LA sample to improve its properties for NLO applications.

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