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Growth and Characterization of Aluminium Nitrate Doped Sulphamic Acid Single Crystal

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ABSTRACT

The search for new NLO materials is a never ending process. Good quality Aluminium Nitrate doped Sulphamic Acid single crystals have been grown by slow evaporation technique. The unit cell parameters of the grown crystals were studied using single crystal XRD. The functional groups present in the grown crystal were identified by FTIR analysis. Optical behaviour of the grown crystal was investigated using UV-Vis-NIR studies. The thermal stability of the grown crystal was confirmed by Thermogravimetric analysis (TGA)/Differential thermogravimetric analysis (DTA). The mechanical strength and Nonlinear optical property of the crystal were determined by Vicker's Microhardness Test and Kurtz powder technique respectively.

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1. Introduction

Nonlinear optical materials have vast application in the field of optoelectronic technology and photonic field. Among the Nonlinear optical materials, single crystals play an important role in the modern technological devices. It was reported earlier that dopants will affect the physical properties of single crystals [1]. Care must be taken in selecting dopants, because some of the impurities will decrease the growth rate of crystals which in turn will modify the physical properties of crystals [2]. Inorganic materials have good optical damage threshold and stability good thermal and mechanical properties have short UV cutoff wavelength and high second order non linearity [3-5]. Among the inorganic materials, Sulphamate derivatives with two planar rings have good blue light transmittance and excellent optical nonlinearity [6-11].

Sulphamic acid is highly stable, soluble in water and exhibits zwitterionic form. It has orthorhombic structure with an annual production of several kilotons [12]. Japanese Industrial Standard, British Analytical methods committee and IUPAC has recommended SA as a standard substance for titrimetric analysis [13]. The growth, structure, UV-Vis-NIR, dielectric studies, FTIR, neutron diffraction and etching and TGA of pure SA were already reported [14-18]. Here we report the growth and characterization of Al(NO₃)₂ doped SA nonlinear optical crystal.

2. Experimental Procedure

 $SA:Al(NO_3)_2$ was synthesized from commercially available SA (Lobachemie AR grade) and Al(NO_3)_2 by slow evaporation method at room temperature. SA and Al(NO_3)_2 was taken in the ratio 1:1 and dissolved in 20ml of double distilled water separately using magnetic stirrer. Both the solutions were mixed together and stirred again to get homogeneous solution. 40ml of final solution was filtered and transferred to a clean beaker. The beaker was covered with perforated aluminium foil to minimize evaporation and the solution was kept in a dust free environment. Good quality single crystals of SA : $Al(NO_3)_2$ were grown in three weeks. The photograph of the grown crystal is shown in Fig 1.



Figure (1). SA: Al(NO₃)₂ crystal. 3. Characterization Techniques

SCXRD analysis is done by BRUKER AXS KAPPA APEX II CCD of the grown crystal. The grown crystal of SA : Al(NO₃)₂ is confirmed by PXRD using BRUKER AXS D8 ADVANCE diffractometer. The incorporation of Al(NO₃)₂ into pure SA is confirmed by FTIR analysis, which is carried out using THERMO NICOLET AVATAR. For Optical analysis, UV-Vis-NIR is done using VARIAN CARRY 300 sSPECTROPHOTOMETER in the wavelength range of 200 nm to 800 nm. Thermal behaviour of grown crystal is analysed between 40 °C and 730 °C in nitrogen atmosphere at a heating rate of 10 °C/min using PERKIN ELMER DIAMOND thermal analysis system. The mechanical strength of the grown crystal is detected by Vicker's Microhardness Tester. SHG property is confirmed by Kurtz powder technique.

4. Results and Discussion

4.1. Single Crystal X-Ray Diffraction Analysis

Single Crystal X-Ray Diffraction is carried out using BRUKER AXS KAPPA APEX II CCD with Shel xtl software. Both Pure SA and SA : $Al(NO_3)_2$ crystallizes into orthorhombic structure. The lattice parameters are given in table (1).The variations in lattice parameters and cell volume of the grown crystal may be attributed to the incorporation of dopants in SA crystal lattice.

Table (1).Lattice parameters of pure & SA : Al(NO₃)_{2.}

Parameter	Pure SA	$SA : Al(NO_3)_2$
$a A^0$	8.100	8.0563
$b A^0$	8.049	8.102
$c A^0$	9.220	9.221
$V A^{03}$	604.8	601.9

4.2. Powder X Ray Diffraction Analysis

Powder X Ray Diffraction analysis of the grown crystal of SA : Al(NO₃)₂ is done using BRUKER AXS D8 ADVANCE Diffractometer and d values are calculated using Difrac Plus software. The grown crystal is scanned for 2θ range of 3 degrees to 80 degrees and is shown in Fig (2). All the observed reflections are indexed. Some extra peaks are observed. The extra peak (013), (103), (032), (044), (015), (035), (600) and (702) in SA : Al(NO₃)₂ are due to the incorporation of Al(NO₃)₂ in to the crystal lattice of pure SA. Change in the intensity of peaks compared to pure SA shows that doping has brought change in the internal structure of the crystal due to the change in the bond length [18]. Welldefined Bragg's peaks at specific 2θ indicate high crystallinity of the grown crystal [12]. The powder X- ray diffractogram of pure and doped SA are shown in Fig (2) and (3).





Characterization of a grown sample is complete with the chemical composition analysis. Fourier Transform Infrared Absorption spectra of SA : $Al(NO_3)_{2}$ is recorded in the range 500 cm⁻¹ to 4000 cm⁻¹ using THERMO NICOLET AVATAR 370. Compared to the absorption band of pure SA, the absorption band of $Al(NO_3)_2$ doped SA becomes narrow in the range 3000 cm⁻¹ to 4000 cm⁻¹.

Change in the absorption pattern of $Al(NO_3)_2$ doped SA is due to the incorporation of the dopant into the pure crystal. The various functional groups present in SA : $Al(NO_3)_2$ are assigned and recorded in the table (2). The FTIR spectrum is shown in Fig (4).



Fig (4).FTIR Spectrum of SA : Al(NO₃)₂ Table (2). Vibrational band assignment for SA : Al(NO₃)₂

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Pure SA	$SA : Al(NO_3)_2$	Assignment	
3211	3152	Degen. NH ₃ ⁺ stretching	
2871	2871	Sym. NH ₃ ⁺ stretching	
1538	1541	Degen. NH_3^+ deformation	
1455	1446	Sym. NH ₃ ⁺ deformation	
1337	1267	Degen. SO ₃ stretching	
1069	1067	Degen. SO ₃ ⁻ deformation	
1001	1005	S - O stretching	
687	690	NH ₂ and N – H wagging	

4.4. UV-Vis-NIR Studies

For practical applications of single crystal, Transmission and Absorption spectra are very important. The crystal should have wide transparency window to be used for opto electronic applications [19], [20]. In the optical transmission studies, transmittance of the grown crystal is examined using VARIAN CARRY 300 SPECTROPHOTOMETER in the wavelength range of 200 nm to 800 nm. It is observed that the lower cutoff wavelength is 261 nm, whereas for pure SA it is 270 nm.



Figure (5). UV- Vis-NIR spectrum of SA: Al(NO₃)₂ crystal.



Figure (6). UV-Vis-NIR spectrum of SA : Al(NO₃)₂ crystal.

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The transmittance spectrum of the grown crystal has a good transmission and less absorption till 800 nm. This shows that the dopant has improved the optical transparency of the grown crystal which makes it a good candidate for opto electronic applications. The UV-Vis-NIR spectrum is shown in Fig (5) and (6).

4.5. TGA/DTA Analysis

The phase transition of the crystal, water of crystallization and different stages of decomposition can be determined from TGA/DTA analysis [21]. TGA/DTA analysis is carried out between 40 °C and 730 °C in nitrogen atmosphere at a heating rate of 10 ⁰C/min using PERKIN ELMER DIAMOND Thermal analysis system. TGA/DTA analysis of SA : $Al(NO_3)_2$ is shown in Fig (7). Initial weight of the sample used for investigation is 8.361g. $SA : Al(NO_3)_2$ undergoes three stages of decomposition on heating. There is no weight loss until 226°C, which shows there is no physically absorbed water in the grown crystal. It can be used for Nonlinear Optical activity until 226°C, where as pure SA decomposes fully at 204°C that corresponds to its melting point [18]. From the sharpness of the peak, the purity and high degree of crystallinity of the grown crystal can be confirmed. The first stage of decomposition occurs at 226°C with a weight loss of 1.37% which may be due to the release of N₂ gas. The second stage of decomposition occurs in the vicinity of 383°C with a mass reduction of 31.77% due to the formation of unstable intermediates with a display of exothermic peak. During the last step of decomposition, the intermediate degrades to metal oxide showing a strong exothermic peak in the range $390^{\circ}C - 450^{\circ}C$.



Figure (7). TGA/DTA of SA : Al(NO₃)₂ crystal. 4.6. Microhardness Study

The microhardness of SA : Al(NO₃)₂ crystal is measured using SHIMADZU MICROHARDNESS TESTER with a diamond intender. Loads of magnitude varying from 25 gm to 100 gm is applied for a fixed interval of time over a wellpolished grown crystal. The Vicker's Microhardness number Hv is calculated using the relation $Hv = 1.8544P/d^2kgmm^2$ ²where P is the applied load in kg and d is the average diagonal length of the indentation in mm. A graph is plotted between Hardness number (Hv) and applied load (P) and is shown in Fig (8). There is an increase in hardness with load which is due to the work hardening of the surface layer. Beyond 100 g, cracking occurs due to the release of internal stresses generated locally by indentation. The increasing value of hardness makes the crystal harder. A graph is plotted with log P and log d which is shown in Fig (9). From the slope of the graph the work hardening coefficient (n) is found to be 4.287. According to Onitsch and Hannemann work hardening coefficient 'n' should lie between 1 and 1.6 for hard materials and above 1.6 for soft materials [22],[23]. Hence the grown crystal is a soft material.



Figure (8). Plot of P Vs Hv of SA: Al(NO₃)₂ crystal.



Figure (9). Plot of log P Vs log d of SA: Al(NO₃)₂ crystal. 4.7. Non Linear Optical study

Kurtz Powder technique is used to test the Second Harmonic Generation of SA : $Al(NO_3)_2$ crystal. Pulse energy is 300 mJS⁻¹ and pulse width is about 10 nS. The bright green emission from the grown crystal confirms second Harmonic Generation. The NLO efficiency of the grown crystal is compared with the standard KDP crystal and is found to be 0.72 times that of KDP crystal.

5. Conclusion

In this investigation, single crystals of Al(NO₃)₂ doped SA are grown by slow evaporation technique at room temperature. XRD analysis confirms the grown crystal possess orthogonal structure. FTIR confirms the presence of all functional groups in the grown crystal. UV-Vis-NIR analysis shows the grown crystal has good optical transmission and lower cutoff wavelength. SA: Al(NO₃)₂ crystal is thermally stable upto 226 ⁶C. From Vicker's Microhardness studies it is found that the grown crystal is a soft material and the hardness of the material increases with load until 100 gm. The dopant has induced NLO property to the grown crystal.

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