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RESEARCH ARTICLE

GROWTH AND CHARACTERIZATION OF AMMONIUM CHLORIDE DOPED SULPHAMIC ACID SINGLE CRYSTAL

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ABSTRACT

Slow evaporation technique has been used to grow ammonium chloride doped sulphamic acid single crystal. Unit cell parameters of the grown crystal were confirmed by single crystal X ray diffraction. FTIR study was carried out to identify the various functional groups present in the grown crystal. Optical and thermal behaviour of the grown crystal were investigated using UV-Vis-NIR studies and thermogravimetric analysis (TGA)/differential thermogravimetric analysis (DTA) respectively. The mechanical strength of the crystal is determined by Vicker's Microhardness Test. Nonlinear optical property was identified by Kurtz powder technique.

INTRODUCTION

Crystal growth of nonlinear optical materials has attracted much attention due to its importance in the emerging optoelectronic technology and photonic field. Single crystals play an important role in the modern technological devices. Dopants affecting the physical properties of single crystal were reported earlier [1]. Some of the impurities will decrease the growth rate of crystals. So, care must be taken in selecting dopants that will modify the physical properties of crystals [2]. When compared to organic materials, inorganic materials have good thermal and mechanical properties; have short UV cutoff wavelength and high second order non linearity; good optical damage threshold and stability [3-5]. Among the inorganic materials, Sulphamate derivatives have good blue light transmittance and excellent optical nonlinearity. Its configuration with two planar rings is most suitable for NLO property [6].

Sulphamic acid is a classical inorganic compound with an annual production of several kilotons [7]. SA has orthorhombic structure. It is highly stable and soluble in water and exhibits zwitterionic form. British Analytical methods committee, IUPAC and Japanese Industrial Standard has recommended SA as a standard substance for titrimetric analysis [8]. The growth, structure, FTIR, TGA, neutron diffraction and etching, UV-Vis-NIR and dielectric studies of pure SA were already reported [9-13]. Here we report the growth and characterization of NH_4Cl doped SA nonlinear optical crystal.

Experimental Procedure

SA:NH_4Cl was synthesized from commercially available SA (Lobachemie AR grade) and NH_4Cl by slow evaporation method at room temperature. SA and NH_4Cl 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 at dust free environment. Good quality single crystals of SA:NH_4Cl were grown in three weeks. The photograph of the grown crystal is shown in figure 1.

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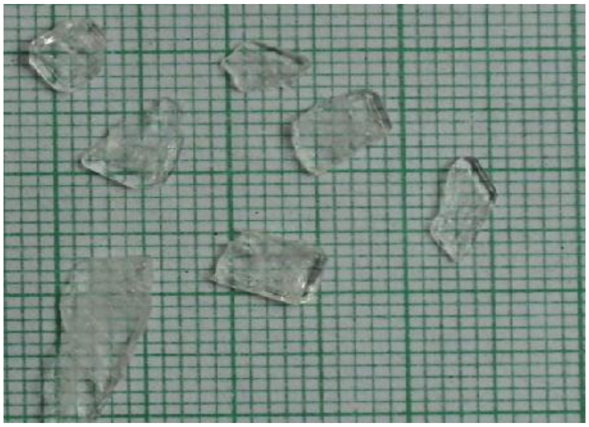

Fig 1 SA:NH_4Cl crystal

Characterization Techniques

SCXRD analysis is done by BRUKER AXS KAPPA APEX II CCD of the grown crystal. The grown crystal of SA:NH_4Cl is confirmed by PXRD using BRUKER AXS D8 ADVANCE diffractometer. The incorporation of NH_4Cl into pure SA is confirmed by FTIR analysis, which is carried out using THERMO NICOLET AVATAR. To study optical property, UV-Vis-NIR analysis is done using VARIAN CARRY 300 SPECTROPHOTOMETER in the wavelength range of 200nm to 800nm. Thermal behaviour of grown crystal is calculated between 40^0C and 730^0C in nitrogen atmosphere at a heating rate of 10^0C/min using PERKIN ELMER DIAMOND thermal analysis system. The mechanical strength of the grown crystal is confirmed by Vicker's Microhardness Tester. SHG property is detected by Kurtz powder technique.

RESULTS AND DISCUSSION

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. Pure SA crystallizes into orthorhombic structure whereas SA:NH_4Cl crystallizes into tetragonal structure. The lattice parameters are given in table (1). The change in the crystal structure is due to the incorporation of dopant into the pure SA crystal.

Table 1 Lattice parameters of pure & NH_4Cl doped SA

Parameter	Pure SA	SA:NH_4Cl
a A^0	8.100	8.0833
b A^0	8.049	8.0833
c A^0	9.220	9.218
V A^{03}	604.8	602.3

Powder X Ray Diffraction Analysis

Powder X Ray Diffraction analysis of the grown crystal of SA:NH_4Cl 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 (030), (023), (014), (005) in SA:NH_4Cl are due to the incorporation of NH_4Cl in to the crystal lattice of pure SA.

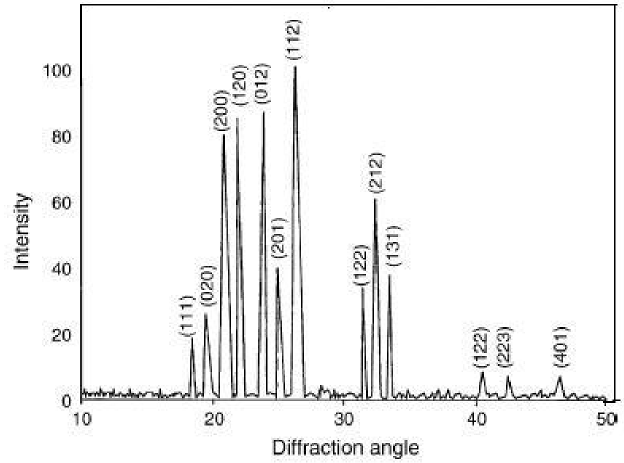

Fig 2 PXRD of pure SA crystal

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 [13]. Well-defined Bragg's peaks at specific 2θ indicate high crystallinity of the grown crystal [7]. The powder X- ray diffractogram of pure and doped SA are shown in Fig(2) and (3).

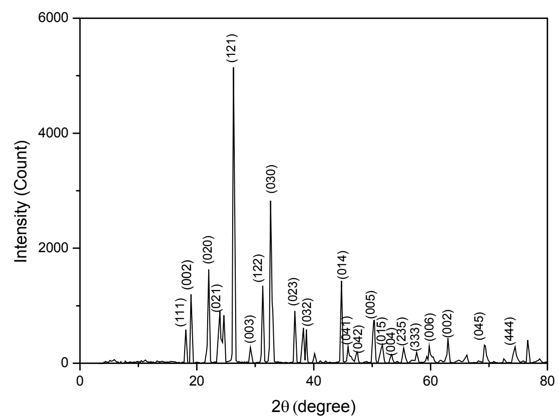

Fig 3 PXRD of SA:NH_4Cl crystal

Fourier Transform Infrared Spectroscopy

Characterization of a grown sample is complete with the chemical composition analysis. Fourier Transform Infrared Absorption spectra of SA:NH_4Cl is recorded in the range 500cm^{-1} to 4000cm^{-1} using THERMO NICOLET AVATAR 370. Compared to the absorption band of pure SA, the absorption band of NH_4Cl doped SA becomes narrow in the range 3000cm^{-1} to 4000cm^{-1}. Change in the absorption pattern of NH_4Cl doped SA is due to the incorporation of the dopant into the pure crystal. The various functional groups present in SA:NH_4Cl are assigned and recorded in the table (2). The FTIR spectrum is shown in fig (4).

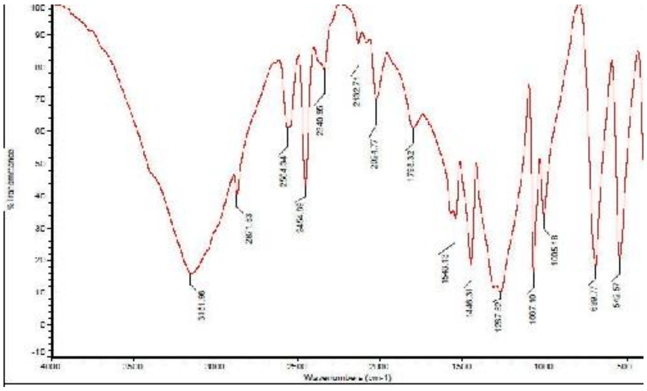

Fig 4 FTIR Spectrum of SA:NH_4Cl

Table 2 Vibrational band assignment for SA:NH_4Cl crystal

Pure SA	SA:NH_4Cl	Assignment
3211	3151	Degen. NH_3^+ stretching
2871	2871	Sym. NH_3^+ stretching
1538	1543	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	689	NH_2 and N – H wagging
539	542	Degen. SO_3^- deformation

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[14, 15]. In the optical transmission studies, transmittance of the grown crystal is examined using VARIAN CARRY 300 SPECTROPHOTOMETER in the wavelength range of 200nm to 800nm. It is observed that the lower cutoff wavelength is 240nm, whereas for pure SA it is 270nm. The transmittance spectrum of the grown crystal has a good transmission and less absorption till 800nm. 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 fig(6).

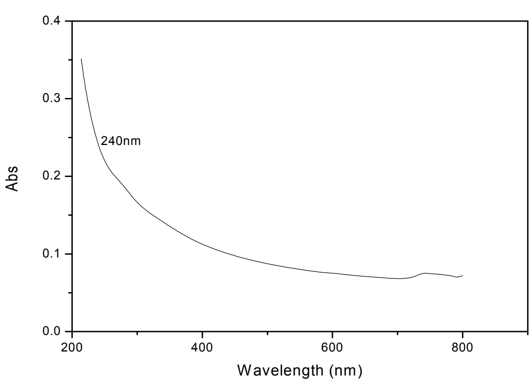

Fig 5 UV- Vis-NIR spectrum of SA:NH_4Cl crystal

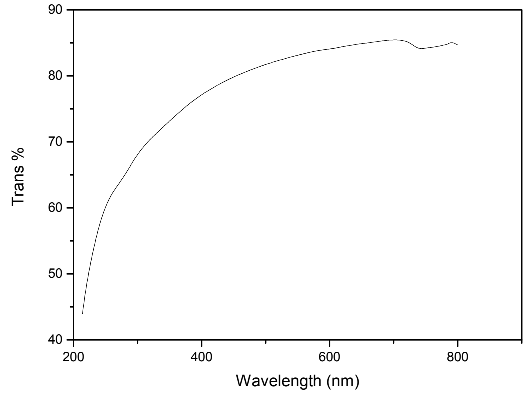

Fig 6 UV-Vis-NIR spectrum of SA:NH_4Cl crystal

TGA/DTA Analysis

The phase transition of the crystal, water of crystallization and different stages of decomposition can be determined from TGA/DTA analysis [16]. TGA/DTA analysis is carried out between 40^0C and 730^0C in nitrogen atmosphere at a heating rate of 10^0C/min using PERKIN ELMER DIAMOND Thermal analysis system. TGA/DTA analysis of SA:NH_4Cl is shown in fig(7). Initial weight of the sample used for investigation is 7.988g. SA:NH_4Cl undergoes double stage of decomposition in the vicinity of 224^0C and 404^0C. There is no weight loss until 224^0C, which shows there is no physically absorbed water in the grown crystal. It can be used for Nonlinear Optical activity until 224^0C, where as pure SA decomposes fully at 204^0C that corresponds to its melting point [13]. From the sharpness of the peak, the purity and high degree of crystallinity of the grown crystal can be confirmed.

From TGA, it is observed that SA:NH_4Cl undergoes two stages of decomposition. The first stage of decomposition occurs at 226^0C with a weight loss of 20.512% of initial mass. The second stage of decomposition occurs in the vicinity of 397^0C with a mass reduction of 76.983%.

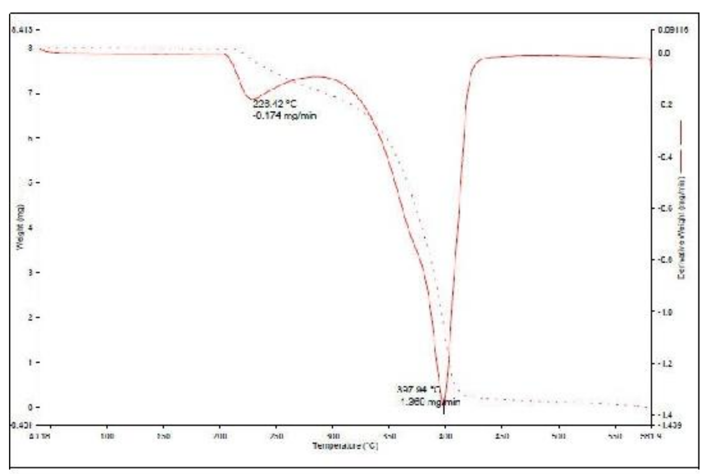

Fig 7 TGA/DTA of SA:NH_4Cl crystal

Microhardness Study

The microhardness of SA:NH_4Cl crystal is measured using SHIMADZU MICROHARDNESS TESTER with a diamond intender. Loads of magnitude varying from 25gm to 100gm is applied for a fixed interval of time over a well-polished grown crystal. The Vicker's Microhardness number Hv is calculated using the relation Hv= $1.8544P/d^2 kgmm^{-2}$ where 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 100g, cracking occurs due to the release of internal stresses generated locally by indentation. The increasing value of hardness makes the crystal harder.

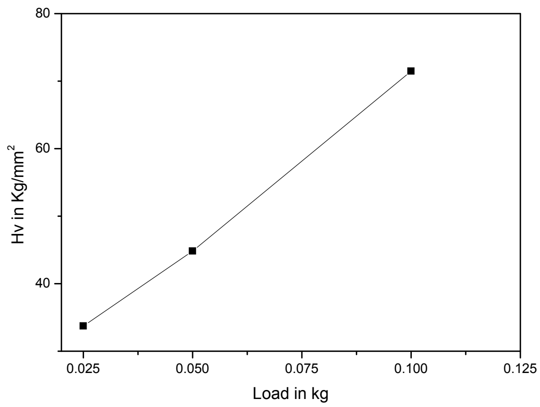

Fig 8 Plot of P Vs Hv of SA:NH_4Cl crystal

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 6.049. 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 [17, 18]. Hence the grown crystal is a soft material.

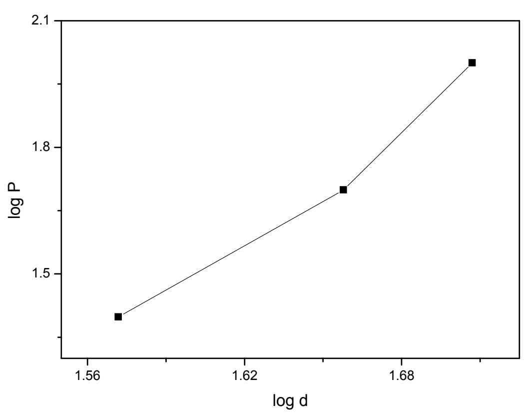

Fig 9 Plot of log P Vs log d of SA:NH_4Cl crystal

Non Linear Optical study

Kurtz Powder technique is used to test the Second Harmonic Generation of SA:NH_4Cl crystal. Pulse energy is $300mJS^{-1}$ and pulse width is about 10nS. The bright green emission from the grown crystal confirms second Harmonic Generation. The NLO efficiency of the grown crystal is 0.63 times that of KDP crystal.

CONCLUSION

In this investigation, single crystals of NH_4Cl doped SA are grown by slow evaporation technique at room temperature. XRD analysis confirms the tetragonal structure of the grown crystal. FTIR confirms the presence of all functional groups in the grown crystal. The grown crystal has good optical transmission and lower cutoff wavelength which is detected by UV-Vis-NIR analysis. SA: NH_4Cl crystal is thermally stable up to 224^0C. From Vicker's Microhardness studies it is found out that the grown crystal is a soft material and the hardness of the material increases with load until 100gm. The dopant has induced NLO property to the grown crystal.

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