



Effect of ZnSO_4 and MnSO_4 on the Growth of Sulphamic Acid Single Crystals

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Abstract

Single crystals of Sulphamic Acid doped with Zinc Sulphate and Manganese Sulphate were grown at room temperature using slow evaporation technique. Structural analysis of the grown crystals was done using single crystal X Ray Diffraction and powder X Ray Diffraction studies. Various functional groups seen in the grown crystals are determined using FTIR spectroscopic analysis. The cut-off wavelength of ZnSO_4 and MnSO_4 doped Sulphamic acid were evaluated by UV-Vis-NIR spectral studies. Thermal behaviour of the grown crystals was identified from Thermogravimetric Analysis (TGA) and Differential Thermogravimetric Analysis (DTA). The mechanical strength and Second harmonic generation of the grown crystals was identified by Vicker's Microhardness Test and Kurtz powder technique respectively.



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Introduction

In the developing field of laser technology and optical communications, the generation of second harmonics is very essential. The search for new Nonlinear Optical materials and enhancing the properties of existing NLO material is a persistent process due to its wide application in the field of science and technology¹. When optical waves propagate through Nonlinear Optical crystal, there should be good transfer of energy between the waves. A Nonlinear Optical crystal should have non zero NLO coefficient, transparency at required wavelengths, high physical

and optical properties to be used in frequency conversion². Inorganic materials have good chemical flexibility, high thermal and mechanical stability and good transmittance³. Among the inorganic materials sulphamate derivatives are most suitable for NLO property with its two planar rings configuration and good blue light transmittance⁴.

Sulphamic acid is a highly stable inorganic acid with orthorhombic structure. Its molecular weight is 97.09¹. It is soluble in water and exhibits zwitterionic form. Large single crystals of pure SA can be grown at

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low temperatures⁵. Due to these characteristics JIS (Japanese Industrial Standard), IUPAC and British analytical methods committee has accepted SA as a standard substance for titrimetric analysis⁶. The growth, structure, UV-Vis-NIR, neutron diffraction and etching, Raman Studies and dielectric analysis of pure SA single crystal is already reported^{1,5,7-10}. Here we report the effect of ZnSO_4 and MnSO_4 in the growth of SA single crystal.

Experimental Procedure

SA: ZnSO_4 (SAZS) and SA: MnSO_4 (SAMnS) were synthesized by slow evaporation method. Analytical grade chemicals were used for the growth of crystals. Zinc Sulphate (4.036 g/20 ml) and Manganese Sulphate (5.033 g/20 ml) along with Sulphamic acid (3.236 g/20 ml) were prepared by mixing them in the ratio 1: 1 using double distilled water and by stirring the saturated solutions for four hours using magnetic stirrer. The final homogeneous solution of 40 ml is filtered twice using micro sized pore whatman No.1 filter paper in to a separate beaker. The beaker was closed tightly with perforated aluminium foil to minimize evaporation and was kept in a dust free, vibration less environment. Good quality single crystals were grown and reystallization process was carried out to improve the purity of the grown

crystals. The photographs of the crystals are shown in figure (1) and (2).

Results and Discussion

Single Crystal X-Ray Diffraction

Single Crystal X-Ray Diffraction is done using BRUKER AXS KAPPA APEX II CCD using $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) with Shelxtl software. Pure SA and ZnSO_4 have orthorhombic structure^{11,12}. When ZnSO_4 is added to pure SA, SAZS crystal has tetragonal structure.

MnSO_4 has Orthogonal Structure¹³. When MnSO_4 is added to SA, SAMnS has tetragonal structure. The addition of dopants has changed the crystal structure of SAZS and SAMnS crystals. The lattice parameters of the grown crystals are tabulated in table (1)

Powder X Ray Diffraction Analysis

Powder X Ray Diffraction analysis of SAZS and SAMnS crystals are done using BRUKER AXS D8 ADVANCE Diffractometer with $\text{CuK}\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation. The grown crystals are crushed into fine powder. The powdered crystals are scanned for 2θ , between 3 degree and 80 degree and shown in Figure (3) and (4). All the observed reflections are indexed. The presence of well defined peaks in the spectrum confirms the high crystallinity of SAZS and



Fig. 1: SAZS crystal

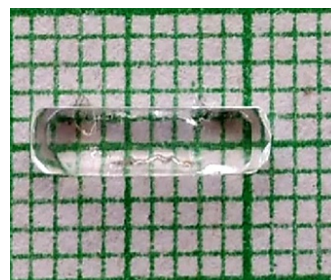


Fig. 2: SAMnS crystal

Table 1: Lattice parameters of SAZS and SAMnS crystals

Parameter/ Grown crystals	a(A°)	b(A°)	c(A°)	V (A° ³)	α (deg)	β (deg)	γ (deg)	Crystal System
SAZS	8.077	8.077	9.267	604.5	90	90	90	Tetragonal
SAMnS	8.0867	8.0867	9.232	603.7	90	90	90	Tetragonal

SAMnScrystals¹⁴. Some extra peaks are observed which are due to the striations in the grown crystals by doping. The change in the intensity of peaks compared to pure SA confirms the incorporation of dopants which had brought changes in the bond length of the grown crystals⁵.

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy identifies the functional groups present in SAZS and SAMnScrystals¹⁵. It is recorded using THERMO NICOLET AVATAR 370 from 500 cm^{-1} to 4000 cm^{-1} . The broad envelope in the region 3750 cm^{-1} -2970 cm^{-1} in pure SA is not observed in SAZS and SAMnS⁹. At 1455 cm^{-1} , the frequency of deformation of NH_3^+ is identified for pure SA, where as it is seen at 1446 cm^{-1} for SAZS and SAMnS¹⁶. The SO_3^- stretching at 1069 cm^{-1} in pure SA is moved to 1066 cm^{-1} for SAZS and SAMnS. Change in the absorption

pattern of the grown crystals is due to the presence of dopants¹⁷. The recorded spectrum is shown in Figure (5) and (6). The functional groups present in SAZS and SAMnS crystals are compared with pure SA and recorded in the table (2).

UV-Vis-NIR Study

Crystals should have wide transparency window to be used for practical applications^{18,19}. Transmittance of the grown crystals are examined from 200 nm to 800 nm using VARIAN CARRY 300 SPECTROPHOTOMETER.

Optical transparency of 94% is observed for SAZS in the wavelength region of 508 nm – 800 nm and the cutoff wavelength is 244 nm. For SAMnS crystal, optical transparency is 95% in the wavelength region of 458 nm – 800 nm and the cutoff wavelength is 213 nm. Both SAZs and SAMnS crystals have good

Table 2: Vibrational band assignment of grown crystals

Pure SA (cm^{-1})	SAZS (cm^{-1})	SAMnS (cm^{-1})	Assignment
3211	3152	3152	Degen. NH_3^+ stretching
2871	2871	2871	Sym. NH_3^+ stretching
1538	1543	1542	Degen. NH_3^+ deformation
1455	1446	1446	Sym. NH_3^+ deformation
1337	1268	1268	Degen. SO_3^- stretching
1069	1066	1066	Degen. SO_3^- deformation
1001	1004	1004	S - O stretching
687	692	691	NH_2 and N – H wagging

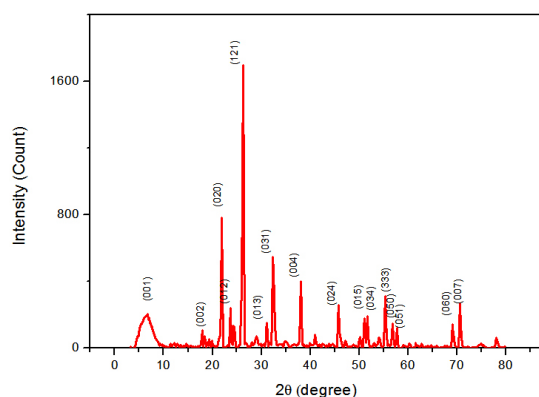


Fig. 3: PXRD of SAZS crystal

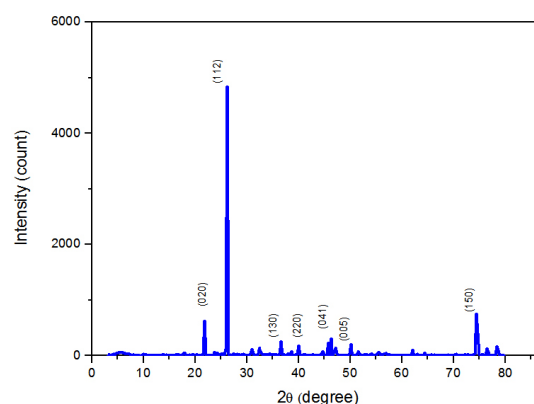


Fig. 4: PXRD of SAMnS crystal

transmittance in the visible region. The grown crystal has less absorption till 800 nm. This shows that the dopant has improved the optical transparency in the visible region of the grown crystal which makes it a good candidate for opto electronic applications²⁰. The UV-Vis-NIR spectrum is shown in Figures (7) - (10).

TGA/DTA Analysis

TGA measures the changes in weight with temperature which can be due to changes in the sample composition and thermal stability²¹. Thermal analysis calculates the maximum temperature with which a material can be utilised^{22,23}. TGA/DTA analysis is carried out using PERKIN ELMER DIAMOND Thermal analysis system in nitrogen

atmosphere between 40°C and 730°C at a heating rate of 100C/min. TGA of grown crystals is shown in Figure (11) and (12).

The TG of the crystal SAZS shows no weight loss upto 227°C which is due to the lack of coordinated water and high stability of the crystal. The weight loss observed at 227°C confirms the melting point of the crystal. The sharp endothermic peak with a weight loss of 79% at 425°C corresponds to the formation of an unstable intermediate ZnH_2SNO_3 . After 500°C, there is a sudden decrease in the decomposition temperature due to the evolution of sulphuric acid. The thermogram of SAMnS shows that there is no decomposition below 100°C, which is due to the

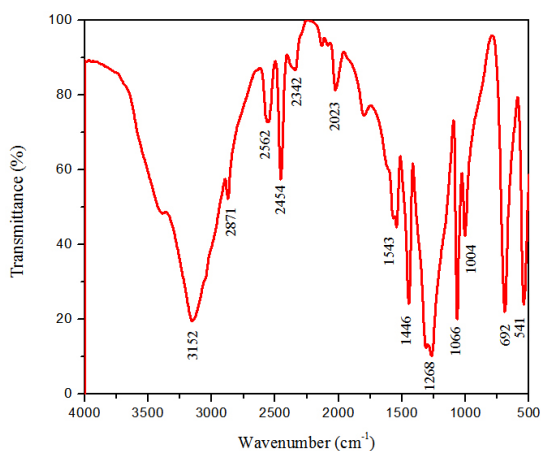


Fig. 5: FTIR of SAZS crystal

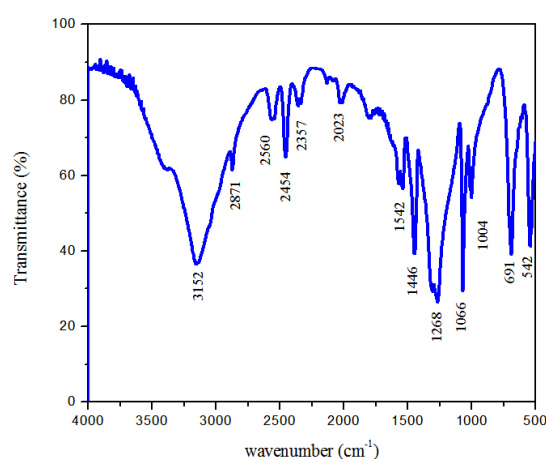


Fig. 6: FTIR of SAMnS crystal

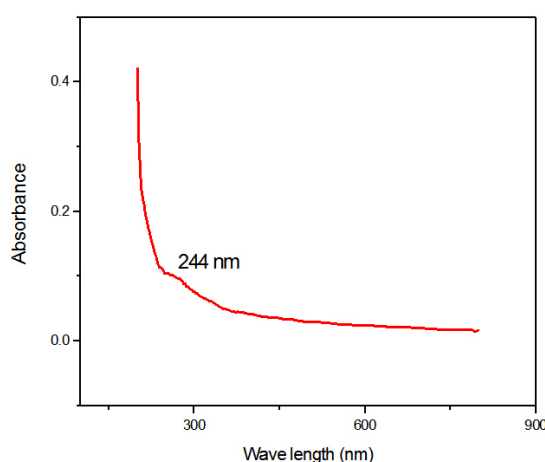


Fig. 7: UV-Vis-NIR Absorption spectrum of SAZS crystal

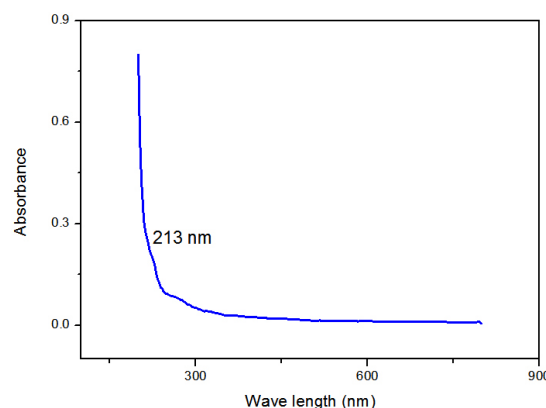


Fig. 8: UV-Vis-NIR Absorption spectrum of SAMnS crystal

absence of water molecule in the crystal. The weight loss at 229°C determines the melting point of the crystal. The sharp endothermic peak with a weight loss of 79% at 431°C is due to the formation of the unstable intermediate MnH_2SNO_3 . The evolution of sulphuric acid corresponds to a sudden decrease in the decomposition temperature after 500°C. From TGA analysis it is clear that this crystal was stable upto 229°C and can be used for Nonlinear Optical activity till 229°C.

Microhardness Study

The microhardness of SAZS and SAMnS crystals are measured using SHIMADZU MICROHARDNESS TESTER with diamond indenter. Loads of magnitude varying from 25 gm to 100 gm 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

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

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 (H_v) and applied load (P) and is shown in Figure (13) and (14). For SAZS and SAMnS crystals, there is an increase in hardness with load which is due to the work hardening of the surface layer²⁴. This proves that these crystals exhibit Reverse Indentation Size Effect (RISE). Beyond 100 g, cracking occurs due to the release of internal stresses generated locally by indentation²⁵. The increasing value of hardness makes the crystal harder.

According to Meyer's law, the relation between the load and size of indentation is given by

$$p = kd^n$$

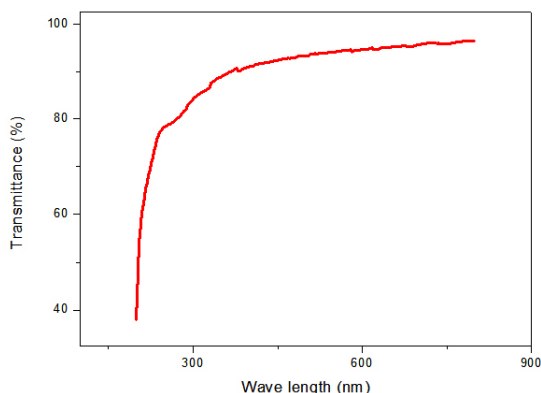


Fig. 9: UV-Vis-NIR Transmission spectrum of SAZS crystal

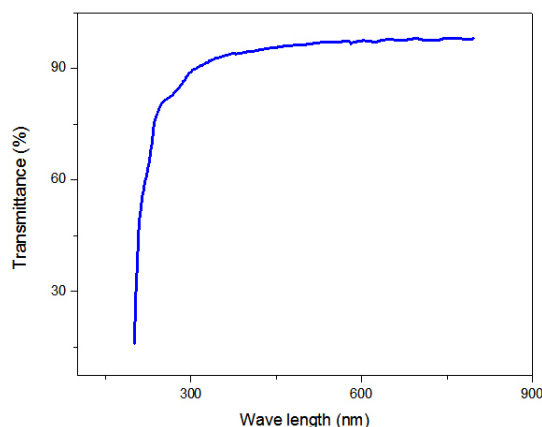


Fig. 10: UV-Vis-NIR Transmission spectrum of SAMnS crystal

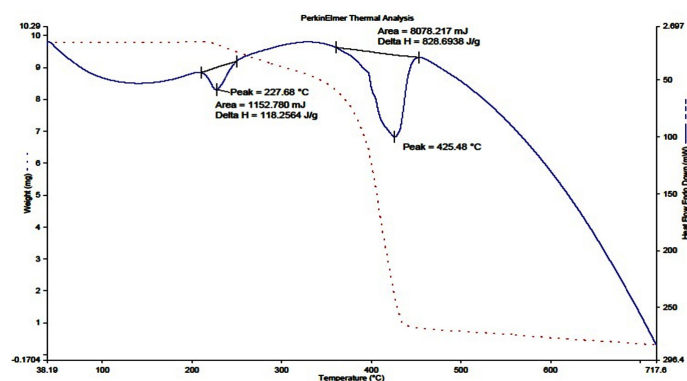


Fig. 11: TGA/DTA of SAZS crystal

where k is the material constant and n is the Meyer's index or work hardening coefficient^{26,27}. A graph is plotted with $\log P$ and $\log d$ which is shown in Figure

(15) and (16). The figure shows a straight line (after least square fitting) and from the slope of the graph the work hardening coefficient (n) is calculated. For

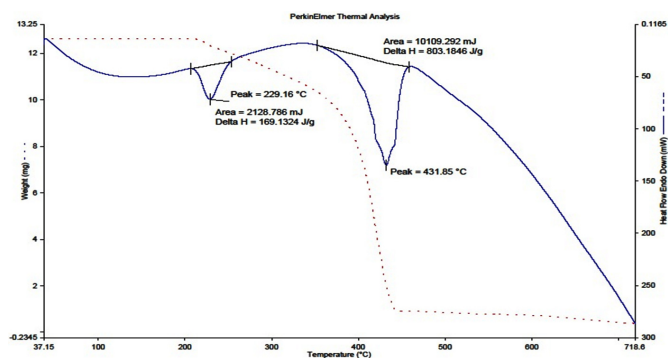


Fig. 12: TGA/DTA of SAMnS crystal

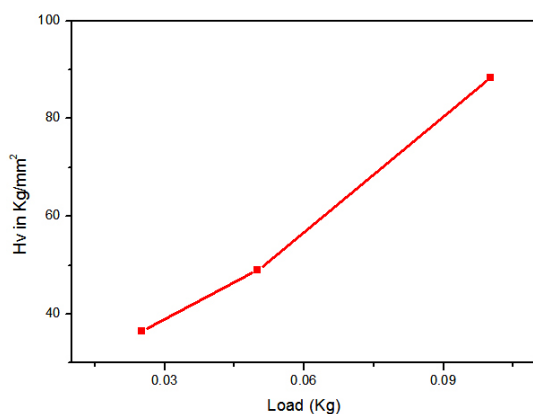


Fig. 13: Plot of HvVs P of SAZS crystal

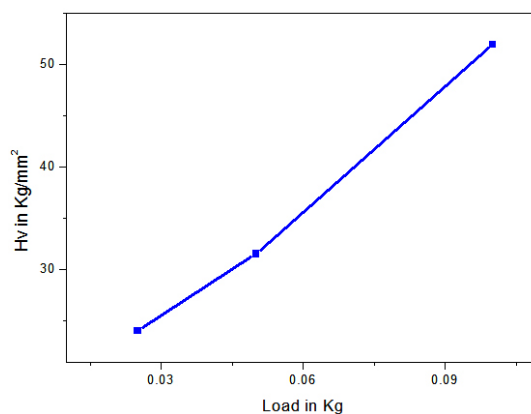


Fig. 14: plot of HvVs P of SAMnS crystal

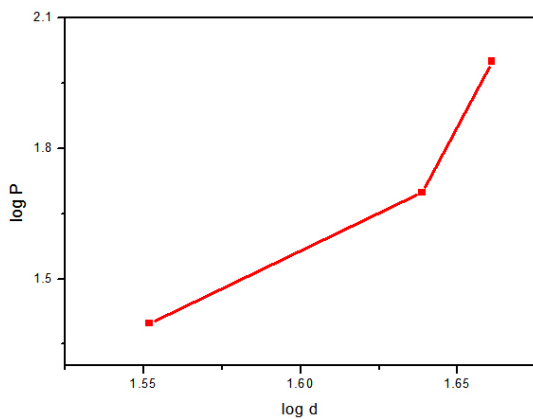


Fig. 15: plot of $\log P$ Vs $\log d$ of SAZS crystal

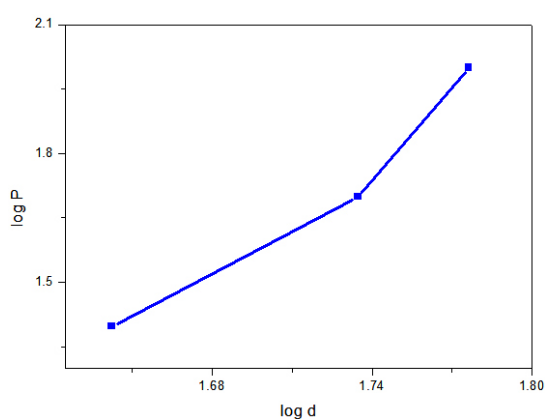


Fig. 16: plot of $\log P$ Vs $\log d$ of SAMnS crystal

SAZS, the work hardening coefficient is found to be 13.514 and for SAMnS it is 7.290. According to Onitsch and Hannemann work hardening coefficient 'n' should be more than 1 and less than 1.6 for hard materials and more than 1.6 for soft materials^{28, 29}. So the grown crystals are soft materials.

Conclusion

SAZS and SAMnS single crystals are grown by slow evaporation solution growth technique at room temperature with aqueous solution. XRD analysis determined tetragonal structure of SAZS and SAMnS crystals. FT-IR analysis confirms the XRD analysis in the form of functional groups present in the grown crystals. Absorption spectrum determines the lower cut off wavelength of 244 nm for SAZS and 213 nm for SAMnS. The presence of dopants has improved the optical property of the grown crystals. Optical studies also confirm the high transparency of SAZS and SAMnS crystals in the visible region. TGA/DTA curves show that all the grown crystals are thermally stable up to 226°C, which is higher than the limit for pure SA. Vicker's Microhardness test

confirms that the grown crystals are soft materials. Hence special care has to be taken during device fabrication using the grown crystals.

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Conflict of Interest

The Authors Declare That There Is No Conflict Of Interests Regarding The Publication Of This Article.

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