# Incorporation of Iron (II) on Structural, Optical, Spectroscopic Studies of Sulphamic Acid Single Crystals

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Abstract: A semi organic Iron (II) doped Sulphamic acid  $(H_2NSO_3H)$  single crystals were grown by slow evaporation Solution Growth Technique. Powder XRD studies were carried out to find crystal structure and lattice parameters of the grown crystals. Functional groups present in the samples and incorporation of metal ion coordination was identified by FTIR spectroscopic analysis. The UV-Vis spectroscopic study reveals that the FeCl<sub>2</sub> doped Sulphamic acid crystal has the lower cut off wavelength was found was found to be 231 nm and has good optical transparency. Second Harmonic Generation (SHG) for the material of this work was confirmed using Nd: YAG laser was presented 1.5 times compared with Potassium Dihydrogen Phosphate (KDP).

Keywords: Growth of Iron(II) Sulphamic single crystal, Functional groups, UV-Vis transparency, SHG.

#### 1. Introduction

The role of bulk crystals in the field of medicine, technology, science has a prominent role [1]. In recent years, inorganic materials have attracted considerable attention [2]. Sulphamic acid (H<sub>2</sub>NSO<sub>3</sub>H) is a very good material, strong and simplest inorganic acid [3-4] to produce semi-organic crystals. Sulphamic acid salts have wide applications as anticorrosive agent [5]. While mixing Sulphamic acid with water it exhibits Zwitterion form [3-4].Recently Spillane and Benson reported review of Sulphamic acid and its Nsubstituted derivatives [6]. The neutron diffraction and X-ray studies confirms (NH; SO) the Zwitterionic structure of the Sulphamic acid crystal [7-10] and also confirm this structure by IR and Raman data [11-15]. For downward growth of a crystal Fe doping was favourable [16-17]. This paper defines the influence and incorporation of metal ion Iron (II) doped in Sulphamic acid (H<sub>2</sub>NSO<sub>3</sub>H) single crystal. The pure and Iron (II) doped Sulphamic single crystals were grown by SEST and have been characterized by the Powder XRD for crystalline nature, incorporation of Fe<sup>2+</sup> ion confirmed by FTIR, the lower UV cutoff wavelength was investigated by the transmittance of electromagnetic radiation and SHG analysis was compared with Potassium Dihydrogen Phosphate (KDP).

#### 2.1. Chemicals used

For the bulk growth of single crystals of title compound Sulphamic Acid (NH<sub>2</sub>.SO<sub>3</sub>H) M.wt: 97.09) g/mol, Ferric Chloride (FeCl<sub>2</sub>.) M.Wt:126.751) g/mol and double distilled water were used for the crystal growth experiment by slow evaporation solution growth technique (SEST) at room temperature.

#### 2.2 . Synthesis and Crystal growth

In the present investigation, the title compound was synthesized by mixing Ferric Chloride (FeCl<sub>2</sub>) and Sulphamic Acid (NH<sub>2</sub>.SO<sub>3</sub>H) were taken in the optimized ratio 1:1 in 100ml double distilled water in a separate 1000ml beaker and stirred well up to 6h continuously to prepare the homogeneous saturated solution using a temperature controlled magnetic stirrer at room temperature by slow evaporation solution growth technique (SEST).

The Chemical reaction of metal ion doped Sulphamic acid given as

$$NH_2SO_3 + FeCl_2 \longrightarrow HO_3S NH_2$$
: FeCl\_2

By using Whattman filter paper the solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation solution growth

#### 2. Experimental

technique at room temperature. After the growth period of 10 to 12 days, bulk single crystals were harvested. The photographs of grown crystals are shown in Fig. 1 &2.

# 3. Characterization studies

The bulk single crystals of pure SA, FeCl<sub>2</sub>.6H<sub>2</sub>O doped SA crystal structure was confirmed by powder XRD analyses was using BRUKER D8 ADVANCE diffractometer. To confirm the incorporation of dopants in the grown crystals, the FT-IR spectra recorded using KBr pellet on Perkin Elmer RXI FTIR spectrometer in the frequency range of 500-4000 cm<sup>-1</sup>.The lower cut off wavelength and the optical transmission spectrum of pure and doped SA grown single crystals were recorded in the wavelength range 200-800 nm using Philips PV8700 UV-visible scanning Spectrometer. The NLO property of the grown crystals was confirmed by Nd: YAG laser.



Figure 1 : Iron (II) doped Sulphamic single crystal



Figure 2: Pure Sulphamic single crystal

# 4. Results and discussion

## 4.1. Powder X-ray diffraction analysis

In the present study improvement in the crystalline quality and structure of the grown crystals Pure and FeCl2 doped SA have been studied by powder X-ray diffraction. The title compound crystallizes in the orthorhombic system. Due to the incorporation of  $Fe^{2+}$  ion in Sulphamic acid the XRD pattern of the crystal shows some extra lines in the crystal and is clear that the variations in lattice parameters. The powder X-ray diffraction pattern of the pure and metal ion doped SA crystallographic data are good agreement with reported values[6] and the Powder XRD pattern are given below in Fig.3.



Fig 3: Powder XRD patterns of pure and doped crystals

# 4.2. FT-IR Spectroscopy

FTIR spectroscopy study is effectively used to identify the functional groups present in the FeCl<sub>2</sub> doped SA crystals were recorded in the range of 500-4000 cm<sup>-1</sup> using KBr pellet on Perkin Elmer RXI FTIR spectrometer are shown in Fig. 4. In pure SA, due to the hydrogen bonding a broad envelope obtained in the region 2970-3431 cm<sup>-1</sup> of asymmetric stretching mode N-H [6] whereas in Fe<sup>2+</sup> doped SA, it is observed in the frequency range 2927-3435 cm<sup>-1</sup>. This broad envelope confirms the metal ion Fe<sup>2+</sup> presence in the Crystal lattice. The peak at 2860cm<sup>-1</sup> for pure and metal ions doped SA is due to N-H· · · O vibration because SA contains five N–H·  $\cdot$  ·O vibrations. The frequency of deformation of NH<sup>3+</sup> was observed in the pure SA at 1463cm<sup>-1</sup> whereas in Fe<sup>2+</sup> doped SA, a slight shift at 1478cm<sup>-</sup> <sup>1</sup>is observed in this peak position. Compared to pure SA this reveals that the incorporation of Fe<sup>2+</sup> dopant disturbed the SA crystal. In pure SA, a broad envelope from 1227 to 1340cm<sup>-1</sup> region and the peak at 1336cm<sup>-1</sup> correspond to the degeneracy of  $SO_3^-$  stretching mode are observed, but in the metal ions doped SA, broad envelope from 1228 to 1395 region and the peak at 1375cm<sup>-1</sup>. The SO<sub>3</sub> symmetric stretching is observed at 1070 dmand rocking mode vibration of  $NH_3^+$  is observed at ~1000cm-1 for pure and metal ions doped SA 1008cm-1 respectively. This NH<sub>3</sub><sup>+</sup> vibration confirms the zwitterionic nature of SA crystal [6]. The SO<sub>3</sub> rocking is around  $697 \text{ cm}^{-1}$ . The band at  $541 \text{ cm}^{-1}$  is

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assigned for SO<sub>3</sub> deformation vibrational mode. The presence of NH, N–S and SO vibrations is also confirmed. The FTIR spectra indicate the incorporation of Fe<sup>2+</sup> ion to the Sulphamic acid occurs through the N ligand at 3138 cm<sup>-1</sup>. The results of normal coordinate analysis and internal modes of Sulphamic acid were confirmed a weakening of the N-S bond and a strengthening of the hydrogen bonding [6]. The functional groups NH, N-S and SO are affected after the incorporation of the Fe<sup>2+</sup> to Sulphamic acid.



 Table 1. Vibrational band assignment for FeCl<sub>2</sub>: SA Single

 crystal

Wavenumber (cm-1)	Assignment
3306	Degen. NH <sub>3</sub> <sup>+</sup> stretching
2866	Sym. NH <sub>3</sub> <sup>+</sup> stretching
1588	Degen. NH <sub>3</sub> <sup>+</sup> deformation
1545	Sym. NH <sub>3</sub> <sup>+</sup> deformation
1478	Degen. SO <sub>3</sub> <sup>-</sup> stretching
1070	SymDegen. SO <sub>3</sub> <sup>-</sup> deformation
1008	Degen. NH <sub>3</sub> <sup>+</sup> Rocking
697	N-S Stretching
541	Degen. SO <sub>3</sub> <sup>-</sup> deformation

#### 4.3. UV-visible spectra

In the UV spectral regions the absence of strongly conjugated bonds of the use of amino acids leads to wider transparency range [18].The UV–Visible transmittance spectrum of pure and the title compound was recorded in solution state in the wavelength range 200–800 nm using Philips PV8700 UVvisible scanning spectrometer and the recorded transmission spectrum is shown in Fig.5. The UV cut off wavelength of pure SA is already reported as 270 nm [18] the cut-off wavelength of FeCl<sub>2</sub> doped Sulphamic acid at 231 nm. It indicates that the incorporation of FeCl2 ion improves optical transmission.



Fig 5: UV-Visible Transmission Spectra of pure and metal ion doped SA

#### 4.4. Second harmonic generation efficiency

The technique for confirming NLO property of Pure and  $FeCl_2$  doped Sulphamic acid crystals was used Second harmonic generation efficiency (SHG) test performed by using the Kurtz-Powder SHG technique. A fundamental wave with a pulse width of 8 ns, energy of the laser pulse around 300 mJ<sup>-1</sup> and a wave length of 1064nm radiated from Nd: YAG laser source was focused on the samples by a lens with focal length of 120 mm [19]. The title crystal FeCl<sub>2</sub> doped SA was powdered with a uniform particle size and densely filled into the quartz cell. The measured SHG efficiency of the doped sample was confirmed by the emission of green



1500 2000

2500

A (Wave Number cm-1)

3000

3500

4000 4500

#### doped SA

0.0

ò

500

1000

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radiation and is compared to the identical size as a reference material with potassium Dihydrogen phosphate (KDP) is 210nm. The NLO efficiency of doped sample was observed 1.5 times the standard KDP and is given in Table 2.There is no emission of green radiation for undoped sample. It can be seen that the dopant modifies some NLO property to the grown sample.

**Table 2:** Measured SHG efficiency of the grown crystals.

Crystal	SHG efficiency	Efficiency with respect to KDP
Pure SA	138	0.98 (~1.000)
FeCl <sub>2</sub> doped SA	210	1.500
KDP	140	1.000

# 5. Conclusion

In the present study Single crystals of pure and FeCl<sub>2</sub> doped SA were grown by slow evaporation solution growth technique (SEST) from aqueous solution at a constant temperature. The structure of grown crystals has been confirmed by using powder X-ray diffraction studies. The FTIR spectra indicate functional groups and the incorporation of Fe<sup>2+</sup> ion to the Sulphamic acid occurs through the N ligand in Sulphamic acid at 3138 cm-<sup>1</sup>. The transmittance of electromagnetic radiation is studied through UV-Visible Spectrum and the lower cut off wavelength was found to be 231 nm. The NLO efficiency of doped sample was observed 1.5 times the standard KDP was confirmed by the Second Harmonic Generation (SHG) studies using Nd: YAG laser.

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# References

- [1] R R.Babu, R.Ramesh, "Growth, structural, spectral, mechanical and optical properties of pure and metal ions doped sulphamic acid single crystals", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol 76(5), pp.470 – 475,2010.
- [2] S.Palaniswamy and O.N.Balasundaram RASAYAN J.ChemVol.2, No.1, pp. 49-52, 2009.
- [3] F.A. Kanda, A.J. King, J. Am. Chem. Soc. 73, 2315, 1951.
- [4] M. SenthilPandian, UritCharoenIn, P.Ramasamy, PrapunManyum, M.Lenin, N.Balamurugan, Journal of Crystal Growth 312, pp.397–401, 2010.
- [5] R.Manickkavachagam, andR K. Rajaram," Crystal

structure of anhydrous sodium sulphamate", Zietschrift für Kristallographie, vol 168(1–4), pp.179–185, 1984.

- [6] P. Muthusubramanian and A. Sundara Raj, *Journal of Molecular Structure*, 84, pp. 25-37, 1982.
- [7] K. Osaki, H. Tadokoro and I. Nitta, Buii. Chem. Sot. Jpn., 28, 524, 1955.
- [8] R. L. Sass, Acta Crystaiiogr., 13, 320, 1960.
- [9]A. F. Cameron and F. D. Duncanson, Acta Crystaiiogr., Sect. B, 32, 1563, 1976.
- [10] J. W\_ Bats, P\_ Coppens and T\_ F\_ Koetzle, Acta Crystailogr., Sect\_ B, 33, 37, 1977.
- [11] S. J. Gupta and A. K. Majumdar, J. hdian Chem. Sot., 18, 457,1941.
- [12] A. M. Vuagnant and E. L. Wagner, J. Chem. Phys., 26, 77.
- [13] I. Nakagawa, S. Mizushima, A. J. Sarceno, T. J. Lane and J. V. Ruagliano, Spectrachim Acta, 12, 239, 1958.
- [14].N. Krishnamurthy, Proc. Indian Acad. Sci., Sect. A, 61 , 146, 1965.
- [15] G. Lucazeau, A. Lautie and A. Novak, J. Raman Spectrosc., 3,161, 1975.
- [16] Y.J. Lai, J.C. Chen, J. Cryst. Growth 212 pp. 211–216, 2000.
- [17] K. Nithya, B. Karthikeyan, G. Ramasamy, K. Muthu, S.P. Meenakshisundaram, Spectrochimica Acta Part A 79, pp.1648–1653, 2011.
- [18]C.Razzetti, M.Ardoino, L.Zanotti, M.Zha, C.Paorici, Soluti ongrowthand characterisation of L-alanine singlecrystals, Cryst.Res. Technol. 37, pp. 456–465, 2002.
- [19] P.Vivek, P.Murugakoothan Advanced Materials Research 584, pp. 51 – 55, 2012.