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Influence of metal ions Mg^{2+}, Fe^{2+} on the growth of Sulphamic acid Single crystals

[1]Rajyalakshmi.S, [2]Brahmaji.B, [3]Samuel.T,[4]Samatha.Kand
[5]Ramakrishna.Yand *[6]Ramachandra Rao.K

Crystal Growth and Nano Science Research Centre
[3,6]Department of Physics, Government College (A) Rajahmundry,
Andhra Pradesh, India
[2]Anil Neerukonda Institute of Tech andScience EngineeringCollege,
Visakhapatnam, India
[1,4]Department of Physics, Andhra University, Visakhapatnam, India
[5]Department of Engineering Physics, Andhra University, Visakhapatnam,India

Abstract: Single crystals of pure and Mg^{2+}, Fe^{2+} ions doped Sulphamic Acid(SA) were grown by conventional technique with dimensions of $16x13x7mm^3$, $9x8x4mm^3$ and $17x16x6mm^3$ respectively. The single crystal X-ray diffraction of pure and Mg^{2+}, Fe^{2+} ions doped SA single crystals confirmed their lattice parameters and crystalized in orthorhombic structure. HRXRD results show that the crystalline perfection of pure and Mg^{2+}, Fe^{2+} ions doped Sulphamic acid single crystals. Mg^{2+} ion doped Sulphamic acid FWHM is more than those of individual grains of pure and Fe^{2+} ion doped SA crystal. The presence of functional groups and the identification of metal ions Mg^{2+}, Fe^{2+} of the dopant were studied using FTIR spectra. The optical transmittance of electromagnetic radiation is studied through UV-Visible Spectrum and the lower cut off wavelength were found to be 221 nm and 231 nm for Mg^{2+} ,Fe^{2+}ion doped SA.The SHG efficiency of the pure and Mg^{2+}, Fe^{2+} ions doped SA crystals have in the order SA > Fe:SA > Mg:SA with the reference of KDP.

Key words: SA, FWHM, HRXRD, SHG.

Introduction

Bulk single crystals plays crucial role of the modern technological devices in the field of science, technology, defense, medicine, and engineering and space sciences [1, 2]. In compared to organic crystals inorganic crystals have optimum thermal and mechanical properties, [3] high mechanical strength, high melting point, high degree of chemical inertness and are widely used for several applications [4]. A strong inorganic Sulphamic acid (H_2NSO_3H) is the mono amide of sulfuric acid which exhibits zwitterionic form while mixing with water [5] and have enormous applications as catalytic, metallurgical and anticorrosive agent for polymer [6]. The single crystal Sulphamic acid growth, structure, neutron diffraction, dielectric studies, UV-vis-NIR spectroscopy, etching and Raman studies were already reported [4, 7-11]. The large size single crystals, growth kinetics, habit modification were influence by the addition of some transition metal ions [12] such as Mg^{2+}, Cu^{2+}, Ni^{2+} with the presence of small amount of impurity plays a vital role[13] due to the development of laser diodes [14-15]. Mg doped bis (thiourea) Cadmium (II) chloride [16, 17] α-$LiIo_3$ [18] were already reported. Large amount of Iron doped $LiNbO_3$ fibers would exhibit larger residual stress and by using polishing and Infrared technique the effect of heavy Fe doped $LiNbO_3$ fibers was investigated [19]. In conventional method extremely the common features of growth impel defect structures composed of growth sector boundaries [20], growth band [21], vacancies, dislocations [22], liquid inclusions [20,23], slip band [24], low angle grain boundaries [25], stacking faults, cracks[26] and twins can be ascribed to impurities. In the present study, we report the influence of metal ions Mg^{2+}, Fe^{2+} on the growth of Sulphamic acid (SA) Single crystals grown by conventional and Sankaranarayanan-Ramasamy techniques.

2. Experimental details

2.1. Synthesis and conventional growth

In the present research Sulphamic acid ($NH_2.SO_3H$), Magnesium chloride hexa hydrate ($MgCl_2.6H_2O$) and ferrous chloride ($FeCl_2$) salts were synthesized using Analar reagent (AR) grade. Millipore water was used as a solvent. The homogeneous saturation solutions of pure SA, Mg^{2+}: SA, Fe^{2+}: SA was prepared by adding 1mol% of $MgCl_2.6H_2O$,$FeCl_2$ at room temperature. The solution was stirred and filtered in a petri dish by using watt men filter paper and kept in a dust-free atmosphere at room temperature.

The chemical reaction of Mg^{2+}: SA given as

$$NH_2SO_3+MgCl_2.6H_2O \longrightarrow HO_3SNH_2: MgCl_2.6H_2O$$

The chemical reaction of Fe^{2+}: SA given as

$$NH_2SO_3+FeCl_2 \longrightarrow HO_3SNH_2: FeCl_2$$

After the growth period of 12 days, pure SA, Mg^{2+}: SA, Fe^{2+}: SA single crystals were harvested with the dimension of 16 x13x7mm^3, 9x8x4mm^3 and 17x16x6mm^3 and the photographs of the grown crystals are as shown in Fig.1(a), Fig.1(b), Fig.1(c).

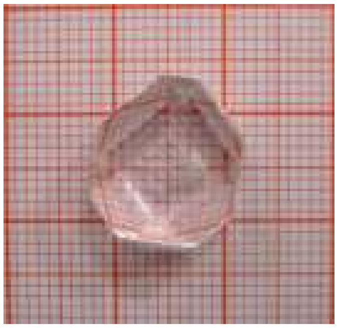

Fig.1 (a): Sulphamic acid

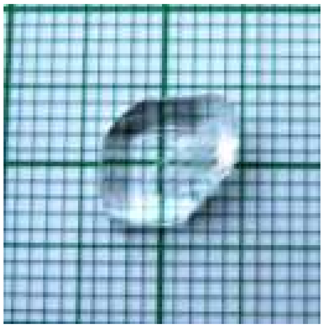

Fig.1 (b): Mg doped Sulphamic acid

Fig.1 (c): Fe doped Sulphamic acid

Typical photographs of Fig.1 (a), Fig.1 (b) and Fig.1(c) Crystals grown by conventional technique

Characterization

3.1 Single crystal X-ray diffraction

Pure Sulphamic acid, metal ions Mg^{2+}, Fe^{2+} doped SA single crystals were subjected to single crystal XRD analysis using Enrafnonius CAD4 X-ray diffractometer to determine the unit cell parameters. The measured cell parameters and HKL index were tabulated in Table 1.The grown crystals pure SA, Mg^{2+}, Fe^{2+} ions doped SA crystals were crystallized in orthorhombic. The discrepancy of 2θ values and lattice parameters in the single crystal XRD may be due to the incorporation of metal ions Mg^{2+}, Fe^{2+} in Sulphamic acid.

Table 1 Single crystal data of pure and Mg^{2+}, Fe^{2+} ions dopes SA crystals.

Sulphamic acid (SA)	**Mg^{2+}: SA crystal**	**Fe^{2+}: SA crystal**
a = 8.09 Å	a = 8.11 Å	a = 8.06 Å
b = 8.12 Å	b = 8.14Å	b = 8.11 Å
c = 9.27Å	c = 9.28Å	c = 9.25 Å
V = 609 Å3	V = 613 Å3	V = 605 Å3
Orthorhombic	Orthorhombic	Orthorhombic
2θ=26.46	2θ=14.23	2θ=19.27

3.2 High-resolution X-ray diffractometry

Fig. 2(a), (b), (c) represents the crystalline perfection of pure and metal ions doped SA single crystals using (100) diffracting planes with a PAN Analytical X'Pert PRO MRD high-resolution X-ray diffraction (HRXRD) system with CuKα_1 radiation.Fig. 2(a) shows the high resolution X-ray diffraction curve recorded by using CuKα_1 radiation for a typical undoped Sulphamic acid (SA) single crystal specimen. As seen in the figure, one can realize that the curve is not a single peak. It is clear that the curve contains two peaks. The additional peak is 23 arc s away from the main peak. This peak corresponds to an internal structural very low angle (tilt angle < 1 arc min) boundary[27] whose tilt angle is 23 arc sec. The FWHM (full width at half maximum) of the main peak and the three low angle boundaries are respectively 10 and 14 arc s. The relatively low values of FWHM of the grains and low angular spread of the DC (~ 100 arc s) specify that the crystalline perfection is quite good. Fig. 2(b) shows the DC recorded for a typical Sulphamic acid crystal doped with $FeCl_2$ are with two peaks. However, the higher FWHM of the individual grains which are 38 and 60 arc sec and the relatively high value of tilt angle i.e. 38 arc sec indicate that due to doping of $FeCl_2$, SA matrix get strained. As seen in the figure 2(c), the specimen Mg doped SA rocking curve (RC) contains a single peak indicates free from structural grain boundaries. The FWHM (full width at half maximum) of the Mg^{2+}: SA curve is 66 arc sec. But when wecompare Mgdoped SAwith pure and Fe doped SA crystals,the FWHM of Mgdoped SAcrystal is more than those of the individual grains of pure and $FeCl_2$ doped SA crystals.

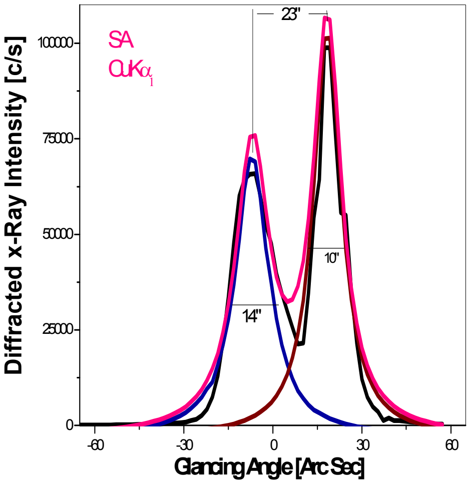

Fig. 2(a): Diffraction curve recorded for typical SA single crystal using (100) diffracting Planes with CuKα_1 radiation

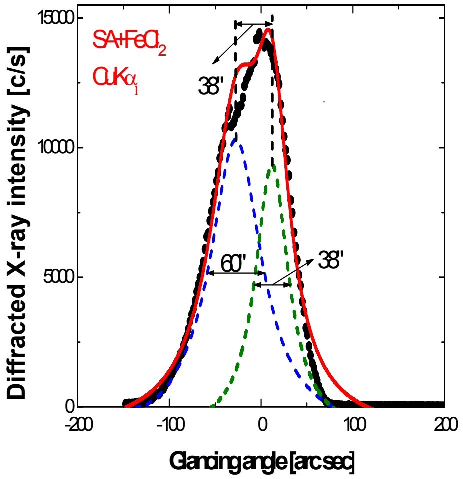

Fig 2(b): Diffraction curve recorded for typical FeCl2 doped SA single crystal using (100) diffracting Planes with CuKa$_1$ radiation

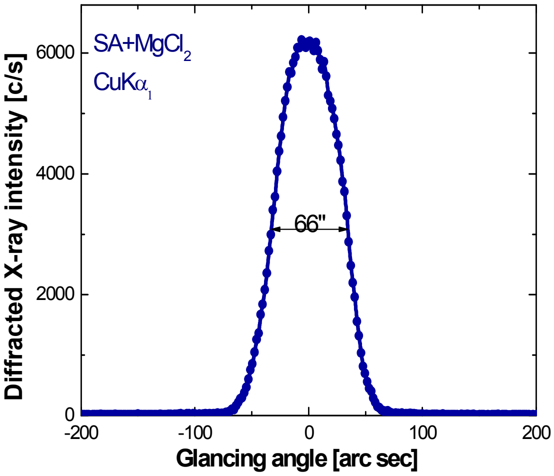

Fig. 2(c): Diffraction curve recorded for a typical MgCl2 doped SA single crystal using (100) diffracting planes with CuKα_1 radiation

3.3 FTIR spectrum analysis

Fourier transform infra-red spectroscopy (FTIR) analysis is used to identify the functional groups of Pure SA, Mg^{2+}: SA and Fe^{2+}: SA single crystals were recorded in the range of 500-4000 cm^{-1} using KBr pellet on Perkin Elmer RXI FTIR spectrometer shown in Fig.3.SA spectrum shows a strong and broad peak from 2970-3431cm^{-1} is due to N-H asymmetric stretching [28] is shifted to 2883–3431cm^{-1} in Mg^{2+}: SA and 2927–3435cm^{-1} inFe^{2+}: SA confirms the incorporation of metal ions in the crystal lattice.In pure specimen the degeneracy of NH_3^+ stretching observed at 3261 cm^{-1} shifted to 3431 cm^{-1}, 3306 cm^{-1} in metal ions doped SA. The medium peak observed at 2872 cm^{-1} is due to NH_3^+ symmetric stretching in pure specimen is shifted to 2908 cm^{-1}, 2866 cm^{-1} in Mg^{2+}, Fe^{2+}: SA. In pure Sulphamic acid S-H stretching observed at 2555 cm^{-1} and shiftedto 2568 cm^{-1} in Mg^{2+}, Fe^{2+}: SA. In pure SA symmetric NH_3^+ deformation observed at 1534 cm^{-1} is shifted to 1545 cm^{-1}, 1588 cm^{-1} in Mg^{2+}, Fe^{2+}: SA. In pure SA degeneracy of SO_3^- stretching observed at 1336 cm^{-1} is shifted to 1370 cm^{-1}, 1395 cm^{-1} in Mg^{2+}, Fe^{2+}: SA. In pure SA symmetric degeneracy of SO_3^- deformation observed at 1063 cm^{-1} is shifted to 1073 cm^{-1}, 1070 cm^{-1} in Mg^{2+}, Fe^{2+}: SA. In pure SA degeneracy of NH_3^+ rocking observed at 1000 cm^{-1} is similar to Mg^{2+}: SA and shifted to 1008 cm^{-1}in $Fe2^+$: SA. In pure Sulphamic acid N-S stretching observed at 690 cm^{-1} is shifted to 701 cm^{-1}, 697 cm^{-1} in Mg^{2+}, Fe^{2+}: SA. The incorporation of Mg^{2+}, Fe^{2+} ions occurs through N-ligand around 3138 cm^{-1} in Sulphamic acid. Due to the incorporation of metal ions in pure specimen the functional groups N-S, SO, NH was influenced.

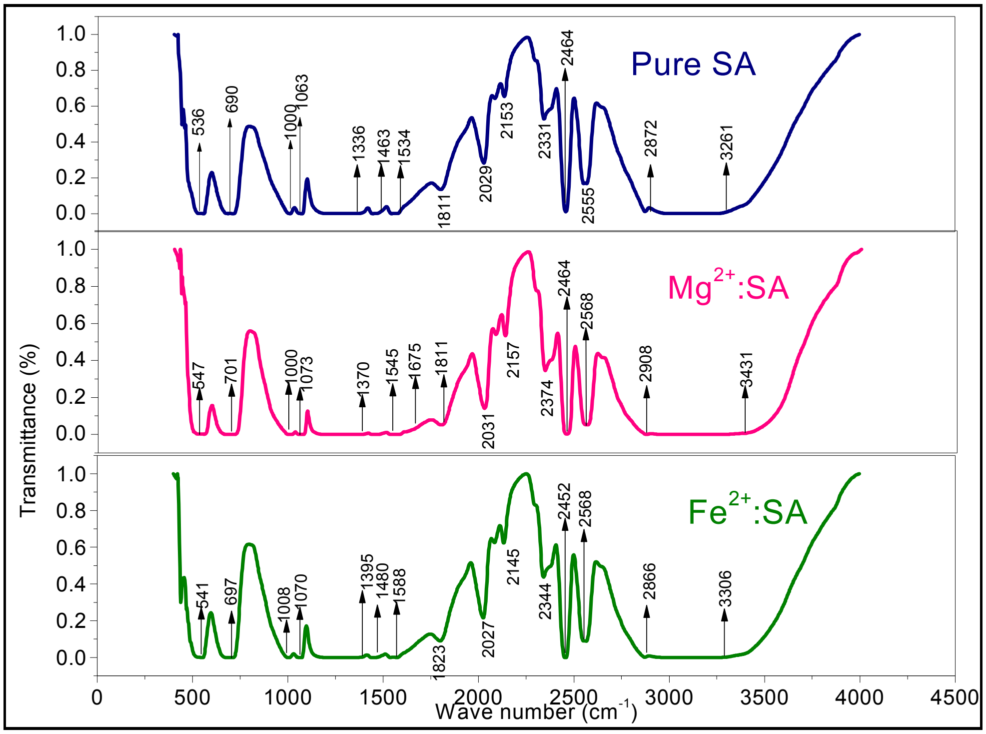

Fig.3. FTIR spectrum of Pure SA, Mg^{2+}: SA and Fe^{2+}: SA

3.4 UV-Vis spectrum analysis

Fig.4 shows the optical transmittance spectrum of pure SA, Mg^{2+}: SA and Fe^{2+}: SA single crystals were recorded using Labindia analytical UV3092 spectrophotometer in the wavelength range of 190-750nm.The lower cut off wavelength of pure specimen is already reported as 270 nm [1] and Mg^{2+}, Fe^{2+}ions doped SAwere found to be 221nm and 231 nm From the spectrum, it is observed that the transmittance ofpure SA, Mg^{2+}: SA and Fe^{2+}: SA grown crystals have 94%, 97%, 96% respectively.Mg^{2+}: SA has good optical transparency than that of pure and Fe^{2+} ion doped Sulphamic acid single crystals. Hence pure and metal ions doped Sulphamic acid single crystals are useful for device applications.

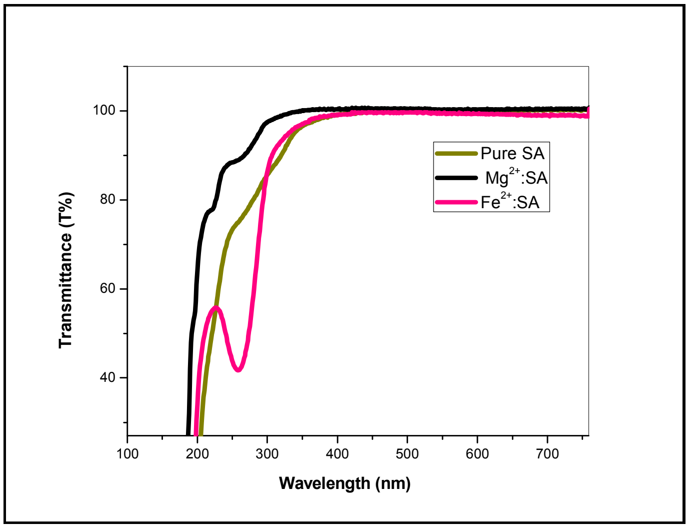

Fig.4. Optical transmittance spectra of Pure and doped Sulphamic Acid Single crystals

3.5 Nonlinear optical studies

The second harmonic generation (SHG) of pure SA, Mg^{2+}: SA and Fe^{2+}: SA crystals was identified by using the Kurtz-powder SHG technique [29].Pure Sulphamic acid, Mg^{2+}, Fe^{2+} ions doped SA were powderedand packed in a one side closed micro capillary tube and exposed to laser radiations was irradiated using the fundamental beam of 1064 nm from Q-switched Nd: YAG laser with the input beam energy of 2.5 mJ/p.The pulse width about 10ns with a repetition rate of 10HZ .No green light emission was observed for pure SA and the second harmonic signals were about 18mV and 15 mV of Mg^{2+}: SA and Fe^{2+}: SA which were about 1.8 and 1.5 times that of KDP confirmed by the emission of green light. The SHG efficiency of the pure and Mg^{2+}, Fe^{2+} ions doped SA crystals have in the order SA > Fe:SA > Mg:SA with the reference of KDP.Hence Mg^{2+}doped SA have good NLO property compared with Pure SA and Fe^{2+} doped SA single crystals.

4. Conclusion

In this study, Pure SA, Mg^{2+}: SA and Fe^{2+}: SAdoped SA single crystals crystalized in orthorhombic structure confirmed by single crystal XRD.Crystalline perfection of the grown crystals were confirmed by HRXRD andthe FWHM of the Mg^{2+}doped SA curve is 66 arc sec which is more than those of the individual grains of pure and Fe^{2+} doped SA single crystals.FTIR analysis confirmed the incorporation of Mg^{2+}, Fe^{2+} ions doped SA occurs through N-ligand around 3138cm^{-1} in Sulphamic acid. The lower cut off wavelength of Mg^{2+}: SA has good optical transparency than that of pure and Fe^{2+} ion doped Sulphamic acid single crystals. The SHG efficiency of Mg^{2+}doped SA crystalwas about 1.8 times that of KDP have good NLO property compared with pureSA and Fe^{2+}: SAsingle crystals

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