

GROWTH AND SPECTROSCOPIC CHARACTERIZATION OF PURE AND UREA DOPED SULPHAMIC ACID SINGLE CRYSTALS

S. RAJYALAKSHMI^a, B. BRAHMAJI^b, K. SAMATHA^a,
K. RAMACHANDRA RAO^c, M.C. RAO^{d*}

^aDepartment of Physics, Andhra University, Visakhapatnam-530003, A.P., India

^bAnil Neerukonda Institute of Tech. and Science Engineering College,
Visakhapatnam-530003, A.P., India

^cCrystal Growth and Nano Science Research Centre,
Department of Physics, Government College (A) Rajahmundry-533105, A.P.,
India

^dDepartment of Physics, Andhra Loyola College, Vijayawad-520008, A.P., India

Single crystals of pure and urea doped sulphamic acid single crystals have been grown from aqueous solution by slow evaporation technique. The influence of urea on the growth of sulphamic acid single crystals was characterized by single crystal X-ray diffraction analysis to determine the lattice parameters. The structure of urea doped sulphamic acid single crystals belongs to orthorhombic system. The crystalline perfection was analyzed by high resolution X-ray diffraction studies. Vibrational modes of pure and urea doped was identified using FTIR spectral analysis. UV-visible spectral studies showed that the transmittance of electromagnetic radiation and the lower cut off wavelength was found to be 235 nm. Second harmonic generation measurement indicate that the efficiency of urea doped sulphamic acid single crystals is nearly equal to KDP crystal.

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1. Introduction

Organic single crystal growth has greatly increased due to their applications in optoelectronics and nonlinear optics. Organic materials lead to growth related problems because of their intrinsic properties such as low thermal conductivity, ease of super cooling and low melting point and weaker mechanical properties [1]. Growth of organic crystal with specific orientation has gorgeous value due to its importance towards device application [2]. Inorganic crystals are extensively used in the applications of optical modulation, fiber optical modulation and optoelectronics [3, 4] due to their high mechanical stability, high degree of chemical inertness and high melting point [5]. To grow bulk single crystals for optoelectronic applications several efforts have been reported in the literature using the Bridgman Stockbarger method [6], Czochralski method [7], solution method [8], vapour method [9] and micro-tube Czochralski method [10,11]. Unidirectional crystal growth technique was reported by Sankaranarayanan and Ramasamy [2] and this method assists growth of bulk size single crystals along a desired orientation for device application. A strong inorganic sulphamic acid (SA) ($\text{H}_2\text{NSO}_3\text{H}$) is the monoamide of sulphamic acid while mixing it with water it exhibits Zwitterionic form [12]. SA salts have large applications as anti-corrosive agent [13]. Urea ($\text{CH}_4\text{N}_2\text{O}$), an organic compound exhibits wide nonlinear optical coefficients, high laser damage threshold and high degree of birefringence [14-17]. The derivatives of urea like 1, 1-dimethylurea ($\text{H}_2\text{NCON}(\text{CH}_3)_2$), monomethylurea ($\text{H}_2\text{-NCONHCH}_3$), phenyl urea ($\text{H}_2\text{NCONHCH}_3$) and 1, 3-dimethylurea ($\text{CH}_3\text{HNCONHCH}_3$) have been examined for NLO applications [18]. Other urea derivatives like urea L-malic acid [19-21] and urea L-tartaric acid

* Corresponding author: raomc72@gmail.com

[22] are of high second harmonic generation (SHG) efficiency and suitable for NLO applications. N-Methylurea ($\text{H}_3\text{CNHCONH}_2$) is one of the organic NLO materials for ultraviolet conversion [23]. In the present study, we report the incorporation of urea in SA single crystals grown by conventional technique from aqueous solution. The grown single crystals have been subjected to single crystal XRD analysis for structure confirmation and to determine lattice parameters. HRXRD, FTIR, UV-Vis and SHG have been used to evaluate the crystalline perfection, vibrational modes, optical and nonlinearity assessment respectively.

2. Experimental

2.1 Growth of urea doped SA single crystal

Urea doped SA was carried out by conventional techniques. Urea: SA was synthesized in equimolar ratio with Millipore water to obtain homogeneous mixture at room temperature. The synthesis was carried out using the reaction



Urea doped SA seed crystal was collected from conventional growth method at room temperature.

2.2 Conventional growth

Urea and SA were taken in equimolar ratio and dissolved in Millipore water. The solution was stirred up to saturation state. The solution was filtered by using watt men filter paper and transferred to petri dish and covered with dust free polyethylene sheet then placed at room temperature. After a period of 24 days good transparent urea: SA single crystal with dimension of about $20 \times 11 \times 5 \text{ mm}^3$ was harvested by spontaneous nucleation. Microbial growth is possible when crystal growth takes longer time to crystallize in amino acids at room temperature [23]. No microbial contamination is observed in the urea: SA growth solution even when solution is kept for more than a month. The photograph of the as grown single crystal is shown in Fig. 1 (a) and Fig.1 (b).

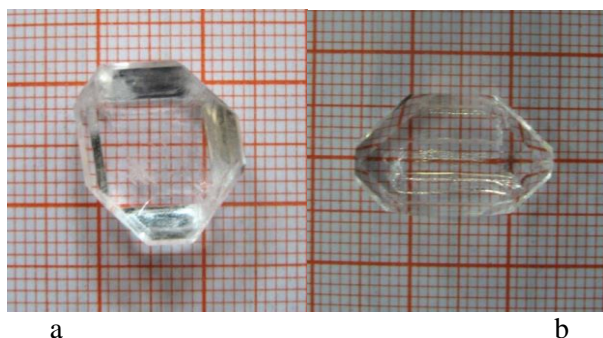


Fig. 1(a) Pure SA single crystal and Fig. 1(b) Urea: SA single crystal

The grown crystals of Urea: SA was characterized by single crystal XRD analysis was carried out using Enraf Nonius CAD4 single crystal X-ray diffractometer. To assess the crystalline perfection of the grown crystal high resolution X-ray diffraction analysis was carried out using a PAN AlyticalX'Pert PRO MRD HRXRD system with $\text{CuK}\alpha_1$ radiation. Functional groups of the grown crystals were carried out by using a KBr pellet Elmer RXI FTIR spectrometer. The optical transmittance spectrum was measured by Labindia analytical UV3092 spectrophotometer. The nonlinear optical efficiency of the crystal has been confirmed by using a Q-switched Nd: YAG laser by employing Kurtz powder technique.

3. Results and Discussion

In this study the Urea: SA single crystal is grown by conventional method. The grown crystals were characterized by the single crystal XRD, HRXRD, FTIR, UV-Vis and SHG analysis.

3.1 Single crystal X-ray diffraction analysis

The grown pure and urea doped SA single crystals were subjected to single crystal X-ray diffraction studies using Enraf Nonius CAD4 single crystal X-ray diffractometer with an incident $M_oK\alpha$ radiation. The above study revealed that the crystal belongs to orthorhombic system. The discrepancy of 2θ values and lattice parameters in the single crystal XRD may be due to the incorporation of urea in SA. The cell parameters were shown in Table-1.

Table1. Single crystal data of pure and UREA: SA single crystals

Crystal	SA	Urea: SA
Crystal System	Orthorhombic	Orthorhombic
a (\AA^0)	8.09	8.19
b (\AA^0)	8.12	8.33
c (\AA^0)	9.27	9.40
v (\AA^3)	609	642
$\alpha=\beta=\gamma$ (deg)	90.00 ⁰	90.00 ⁰
2 θ	26.46	68.90

3.2 High resolution X-ray diffraction analysis

The crystalline perfection of pure and Urea: SA crystal was characterized by high-resolution X-ray diffraction (HRXRD) by employing with a PAN Analytical X'Pert PRO MRDHRXRD system with $CuK\alpha_1$ radiation. Fig. 2(a) and Fig. 2(b) show the high-resolution diffraction curve recorded for (1 0 0) diffraction planes for undoped and urea doped SA single crystals. As seen in the Fig. 2(a) for the pure SA, the curve is not having a single diffraction peak. It is clear that the curve contains two peaks. The peak corresponds to an internal structural very low angle (tilt angle < 1 arc min) boundary [24]. The FWHM (full width at half maximum) of the main peak and the low angle boundaries are respectively 10 and 14 arc s. The structural grain boundary is 23 arc s from its adjoining region. The low values of FWHM of the grains specify that the crystalline perfection is reasonably good. From Fig. 2(b), in title compound the absence of additional peaks and a sharp DC show the crystalline perfection of the specimen crystal is good and indicates free from structural grain boundaries. The FWHM of the Urea: SA curve is 56 arc s. When we compare FWHM of Urea: SA is more than that of the individual grains of the pure SA single crystals.

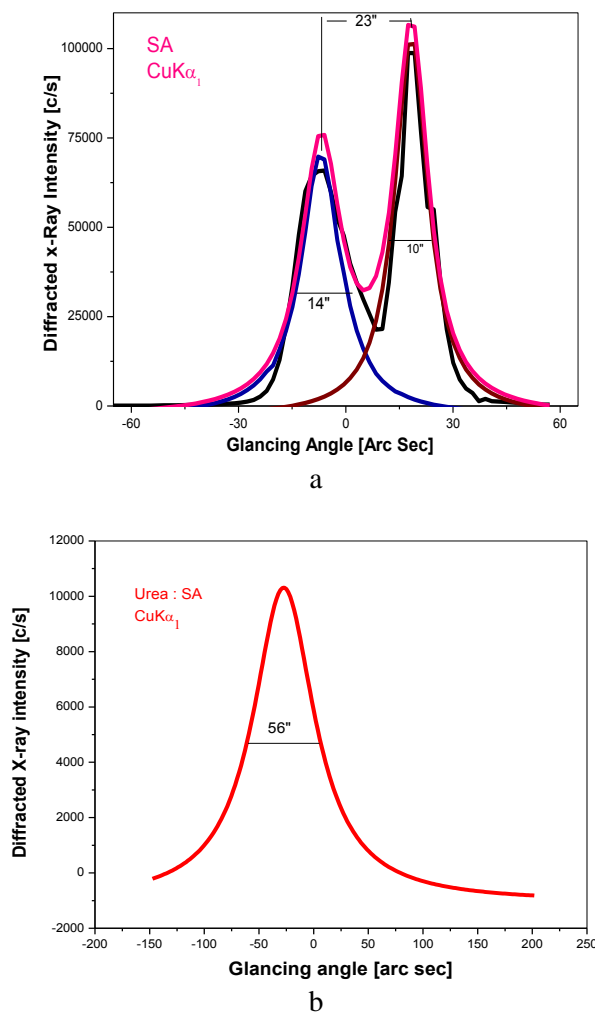


Fig. 2(a) Diffraction curve of SA single crystal using (100) diffracting planes with $\text{CuK}\alpha_1$ radiation; (b) Diffraction curve of Urea:SA single crystal using (100) diffracting planes with $\text{CuK}\alpha_1$ radiation

3.3 FT-IR analysis

Fig. 3 shows the FT-IR spectra of pure and urea doped SA single crystal. The spectra were recorded in the range $500\text{--}4000\text{ cm}^{-1}$ using a KBr pellet Elmer RXI FTIR spectrometer. In the FTIR spectrum of undoped SA, a strong and broad peak from $2970\text{--}3431\text{ cm}^{-1}$ is due to N-H asymmetric stretching [25]. In Urea:SA, this peak is shifted to $2847\text{--}3451\text{ cm}^{-1}$, confirming the incorporation of urea in the crystal lattice. The frequency assignments of the expected functional groups were tabulated in Table-2. The incorporation of urea occurs through N-ligand around 3140 cm^{-1} in SA. Due to the incorporation of urea in the pure specimen, the functional groups N-S, SO, and NH were influenced.

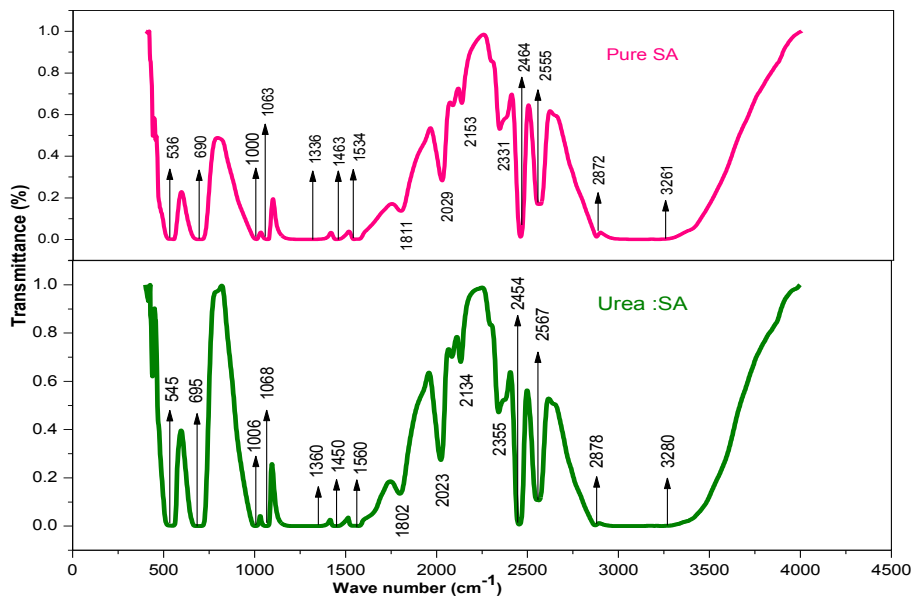


Fig. 3 FTIR spectrum of pure and Urea: SA single crystal

Table-2 Functional groups of pure and Urea: SA single crystals

Pure SA	Urea: SA	Assignments
3261	3280	Degen. NH_3^+ stretching
2872	2878	Sym. NH_3^+ stretching
2555	2567	S-H stretching
2464	2454	S-H stretching
1534	1560	Degen. NH_3^+ deformation
1463	1450	Sym. NH_3^+
1336	1360	Degen. SO_3^- stretching
1063	1068	Degen. SO_3^- deformation
1000	1006	Rocking mode NH_3^+
690	695	NH_2 and N-H agging
536	545	Degen. SO_3^- deformation

3.4 UV-vis transmission spectrum

The optical transmittance spectrum of the grown crystals pure and urea doped SA was measured by Labindia analytical UV3092 spectrophotometer to know the stability for optical application. From the spectrum (Fig. 4) it is observed that the transmittance of pure SA and urea doped SA grown crystals have 96% and 93% respectively. The lower cut off wavelength of SA was reported as 270 nm [26] and urea doped SA was found to be around 235 nm due to the influence of dopant.

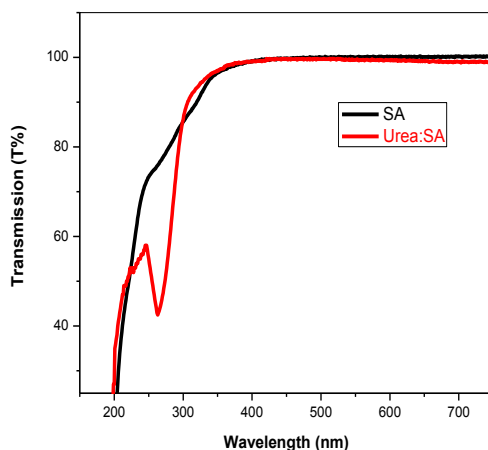


Fig. 4 UV-Vis transmission spectrum of pure and Urea: SA single crystal

3.5 Second harmonic generation (SHG) property study

The SHG property in urea doped SA powdered sample was studied using Q-switched Nd: YAG laser by employing Kurtz powder technique [27]. The SHG measurement was carried out using Q-switched mode locked with wavelength at 1064 nm, with the input beam energy of 2.5 mJ/p and a pulse width of 8 ns at a repetition rate of 10 Hz. The standard KDP crystal gave an SHG of 10 mV/pulse. The second harmonic signal was about 11 mV which was approximately equal to KDP crystal as a reference material from the same input energy. There was no green light emission was observed for pure SA. Hence it was confirmed that the grown specimen have NLO efficiency approximately equal to KDP.

4. Conclusions

Good quality single crystal of urea: SA has been grown by conventional slow evaporation solution growth techniques from aqueous solution. Its lattice dimensions have been calculated from single crystal XRD analysis. From the high-resolution X-ray diffraction studies, the structural perfection of the grown crystal was identified. The incorporation of urea occurs through N-ligand around 3140 cm^{-1} in SA. Its optical transparency has been assessed by UV-Vis spectroscopy and the cut off wavelength was found to be around 235 nm. It is observed that SHG efficiency of Urea: SA has approximately equal to KDP.

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References

- [1] K. Sankaranarayanan and P. Ramasamy, J. Cryst. Growth **193**, 252 (1998).
- [2] K. Sankaranarayanan and P. Ramasamy, J. Cryst. Growth **280**, 467 (2005).

- [3] D. Yu and D. Xue, *Acta Cryst. B* **62**, 702 (2006).
- [4] D. Xue and S. Zhang, *Physica B: Condens. Matt* **262**, 78(1999).
- [5] K. Li, X. Wang, F. Zhang and D. Xue, *Phys. Rev. Lett.* **100**, 235504 (2008).
- [6] M. Arivanandhan, K. Sankaranarayanan, K. Ramamoorthy, C. Sanjeeviraja and P. Ramasamy, *Cryst. Res. Tech.***39**, 692(2004).
- [7] J. Bleay, R.M. Hooper, R.S. Narang and J.N. Sherwood, *J. Cryst. Growth* **43**, 589(1978).
- [8] H.G. Gallagher, R.M. Vrcelj and J.N. Sherwood, *J. Cryst. Growth* **250**, 486 (2003).
- [9] D. Haarer and N. Karl, *Chem. Phys. Lett.* **21**, 49 (1973).
- [10] M. Arivanandhan, K. Sankaranarayanan, C. Sanjeeviraja, A. Arulchakkaravarthi, P. Ramasamy, *J. Cryst. Growth***281**, 596(2005).
- [11] K. Sankaranarayanan and P. Ramasamy, *J. Cryst. Growth***193**, 252(1998).
- [12] F.A. Kanda and A.J. King, *J. Am. Chem. Soc.* **73**, 2315 (1951).
- [13] R. Manickavachagam and R. K. Rajaram, *Zeitsc. für Kristallographie* **168**(1-4), 179 (1984).
- [14] K. Cheng, W.R. Bosenberg and C.L. Tang. *Prog. Cryst. Growth Charact.***20**, 9 (1990).
- [15] W.R. Donaldson and C.L. Tang. *Appl. Phys. Lett.***44**, 25 (1984).
- [16] G.C. Catella, J.H. Bohn and J.R. Luken. *IEEE J. Quantum Electron.* **24**, 1201 (1988).
- [17] T. Rajalakshmi, R. Dhanasekaran and P. Ramasamy. *J. Mater. Sci. Lett.* **12**, 1797 (1993).
- [18] M. Ardoino, L. Zeng, C. Razzetti, M. Zha, L. Zanotti and M. Curti, *Mater Chem Phys.* **66**, 299 (2000).
- [19] E. de Matos Gomes, V. Venkataramanan, E. Nogueira, M. Belsley, F. Proenc, A. Criado, M.J. Dianez, M.D. Estrad and S. Perez-Garrido. *Synth. Met.* **115**, 225 (2000).
- [20] A. Deepthy, S. Vanishri, D. Ambika, D. George Sajan, VPN. Nampoore, HL. Bhat, E. de M. Gomes, M. Belsley. *Mater. Res. Bull.* **43**, 1641 (2008).
- [21] V.K. Dixit, S. Vanishri, H.L. Bhat, E. de Matos Gomes, M. Belsley, C. Santinha, G. Arunmozhi, V. Venkataramanan, F. Proena and A. Criado. *J. Cryst. Growth* **253**, 460(2003).
- [22] P. Santhana Raghavan, P. Ramasamy, *Rec. trends in cryst. Growth.* **68**, 235 (2002).
- [23] M. Shimizu, M. Tachibana, K. Inoue, K. Kojim, *Melt. J. Cryst. Growth*, **177**, 135 (1997).
- [24] G. Bhagavannarayana, R.V. Ananthamurthy, G.C. Budakoti, B. Kumar, K.S. Bartwal, *J. Appl. Cryst.* **38**, 768 (2005).
- [25] P. Muthusubramanian and A. Sundara Raj, *J. of Mol. Struct.* **84**, 25 (1982).
- [26] R. Ramesh Babu, R. Ramesh, R. Gopalakrishnan, K. Ramamurthy, G. Bhagavannarayana, *Spectrochim. Acta Part A* **76**, 470 (2010).
- [27] S.K. Kurtz and T.T. Perry, *J. Appl. Phys.* **39**, 3798 (1968).