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Research Article

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Synthesis, growth and characterization of semi-organic nonlinear optical 4-sodium substituted 1,4-but-2-ene-di-oic crystals

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ABSTRACT

Single crystal of 4Sodium substituted 1,4 but-2-ene-di-oic crystals has been grown by slow evaporation method. Single crystal x-ray diffraction analysis shows that it belong to Triclinic system. The presence of functional groups was confirmed by Fourier Transform Infrared Spectroscopy. Optical behavior has been studied by UV-Vis analysis and found that there is no absorption in the entire visible region. The NLO efficiency of the crystal has been confirmed by the Kurtz Perry method using Nd-YAG laser.

Keywords: Growth from solution, Single crystal XRD, FTIR, UV-Vis spectrum, SHG test.

INTRODUCTION

Nonlinear Optics has emerged as the most attractive field of studies in current research in view of its vital applications in areas such as optical modulation, optical switching, frequency conversion, optical disc data storage, laser remote sensing, medical diagnostics etc [1-4]. The study reveals that semi-organic NLO materials possess interesting nonlinear optical properties owing to their large nonlinear coefficient, high laser damage threshold and good mechanical and thermal stability [5-9].

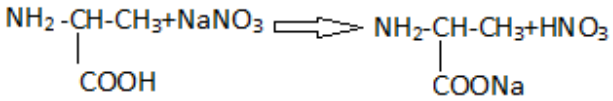
Amino acid family type crystals have over the years been subjected to extensive investigation by the researchers for their high non-linearity and chemical stability. Among the amino acids, L-Alanine (CH_3CHNH_2COOH) is the simplest one with SHG efficiency of about one-third of the well known KDP.L-Alanine Sodium nitrate crystals was reported by Prabha *et al* [10], L-Alanine maleate was studied by Bala Subramanian *et al* [11].L-Alanium maleate crystals was reported by Victor Antony Raj *et al* [12], and Vijayan *et al* [13].Uurea doped L-alaninium maleate crystals was reported by Krishnasamy *et al* [14]. Keeping this in mind, L-alanine, Sodium nitrate, and Maleic acid had been mixed to form a novel Semi organic NLO material. But no other reports on the 4Sodium substituted 1,4 but-2-ene-di-oic crystals are available.4Sodium substituted 1,4 but-2-ene-di-oic crystals are hereafter referred to as ASNMA(Alanine, Sodium Nitrate, Maleic Acid) crystals.

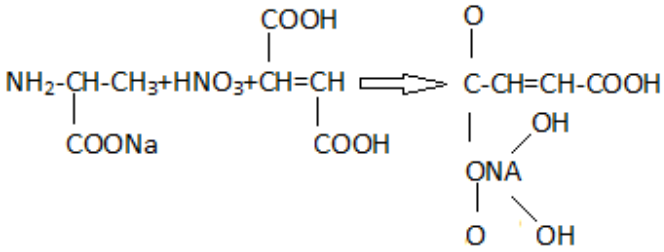
This paper reports the synthesis and characterization studies of ASNMA single crystal grown from aqueous solution. The title compound is subjected to SCXRD and FTIR analysis. UV-vis studies were carried out for the grown crystals. The NLO properties of the ASNMA crystals were investigated by Kurtz and Perry technique.

EXPERIMENTAL SECTION

Synthesis and crystal growth

In the present study, the commercially available Analytical grade(AR grade) L-Alanine(Sigma Aldrich CAS Number 56-41-7), and Sodium nitrate(Sigma Aldrich CAS Number 7631-99-4) were taken in equimolar ratio and dissolved in triple distilled water. The solution was stirred well using a magnetic stirrer for about 3 hours to get homogeneous solution. Thereafter,1 mol % of Maleic acid(Sigma Aldrich CAS Number 110-16-7) is slowly added to the same solution. The chemical reaction is as follows:





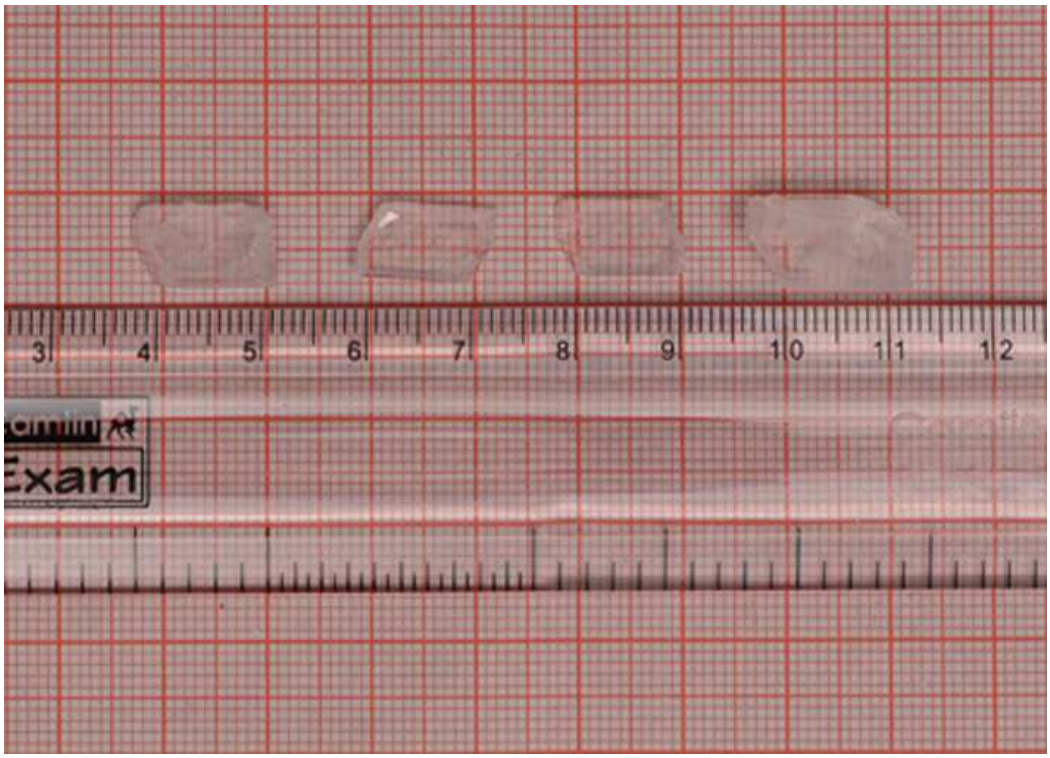


Fig.1.Photograph of grown crystal of ASNMA

After adding Maleic acid, precipitate is formed at the bottom of the beaker. Finally, supernatant liquid alone is filtered by using Whatman filter paper and transferred to a beaker. The filtered solution was covered by perforated sheet and placed in a dust free atmosphere for constant growth. The purity of the synthesized salt was further

improved by successive recrystallization process. A typical single crystal with size 7x5x15 mm^3 was obtained within a period of 25-30 days. Fig 1 shows the photograph of grown single crystals of ASNMA. It is evident from the photograph that the crystals are developed with sharp edges.

RESULTS AND DISCUSSION

Characterization technique

3.1 Single crystal XRD studies

The structural properties of ASNMA, have been studied by single crystal X-ray diffraction studies using Bruker Kappa Apex II diffractometer with Mo Kα(λ = 0.71073 Å) radiation. The structure of the title compound was solved by the direct method and refined by the full matrix least square technique using X SHELL programme. From the data it is observed that it belongs to triclinic system with space group P1 .The lattice parameters are observed to be a = 5.9471 Å b = 6.3876 Å c = 11.2260 Å α=104.191˚β=91.526˚ γ=100.214˚ Fig 2 and 3. represent the molecular structure and ORTEP diagram of ASNMA single crystal. Crystalographic data and structure refinement of ASNMA crystal was provided in Table 1.

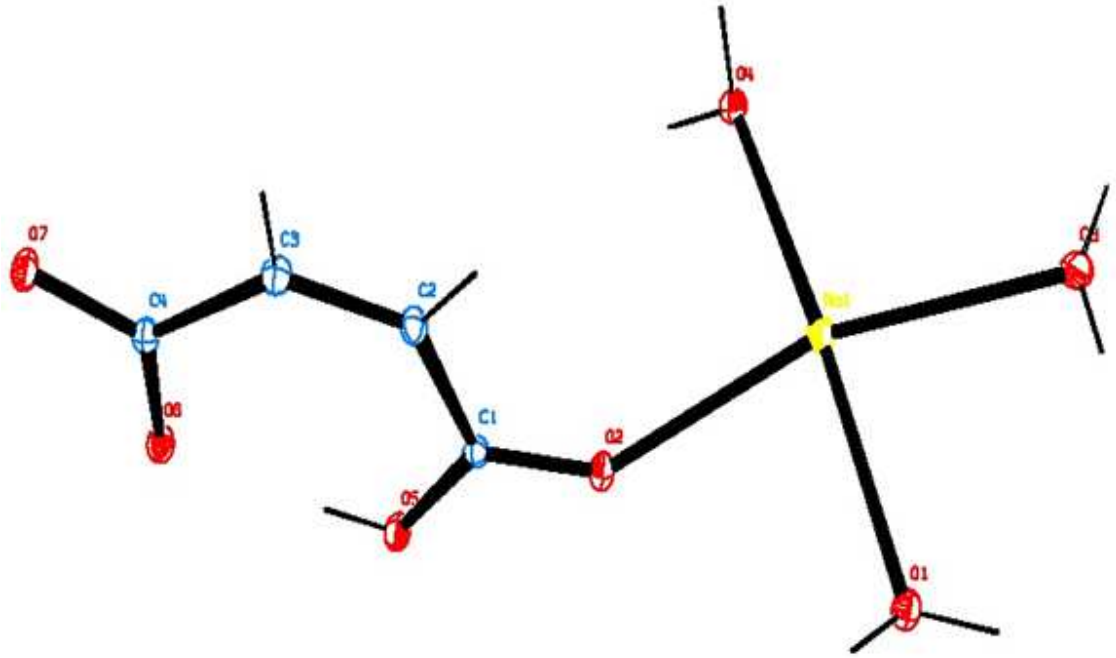


Fig .2. The molecular structure of ASNMA crystal

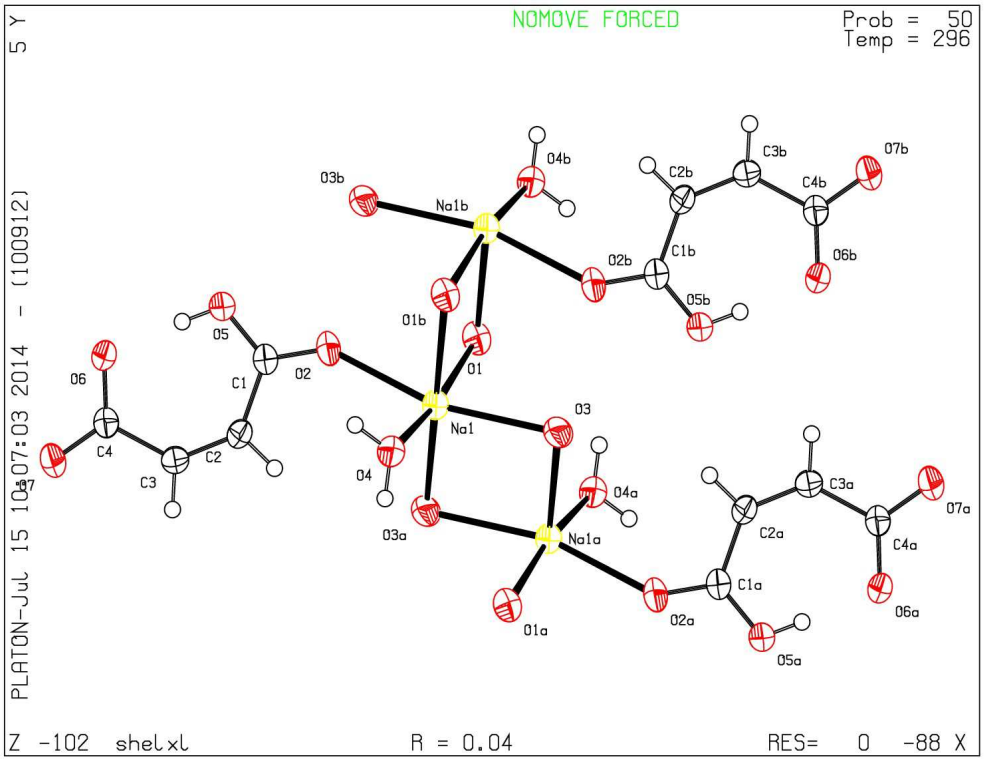


Fig .3. ORTEP of ASNMA crystal

Table 1.Crystalographic data and structure refinement of ASNMA single crystal

Identification code	**ASNMA Crys als**
Empirical formula	$C_4H_5NAO_7$
Formula weight	188.07
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Uit cell dimensions	a=5.9471Å b=6.3876Å c=11.2260Å α=104.191˚ β=91.526˚ ϒ=100.214˚
Volume	405.78
Z	2
Density (calculated)	1.539 mg/m3
Absorption coefficient	0.194 mm-1
Crystal size	0.35 x 0.30 x 0.25 mm
Theta range for data collection	1.88 to 28.24 deg.
Limiting indices	-7<=h<=6, -8<=k<=8, -13<=l<=14
Reflections collected / unique	3151 / 1946 [R(int) = 0.0168]
Completeness to theta	28.24 97.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9532 and 0.9354
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1946 / 1 / 118
Goodness-of-fit on F^2	1.201
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1327
R indices (all data)	R1 = 0.0503, wR2 = 0.1454
Largest diff. peak and hole	0.732 and -0.260 e.A^-3

3.2 FT-IR spectral analysis

FT-IR is an effective tool which provides information about the nature of bonding involved, so that Fourier Transform Infrared Spectrum of ASNMA crystal was recorded in the range of 400 cm^{-1} to 4000 cm^{-1} using Thermo Nicolet, Avator 370.The resulting spectrum is shown in Fig.4.

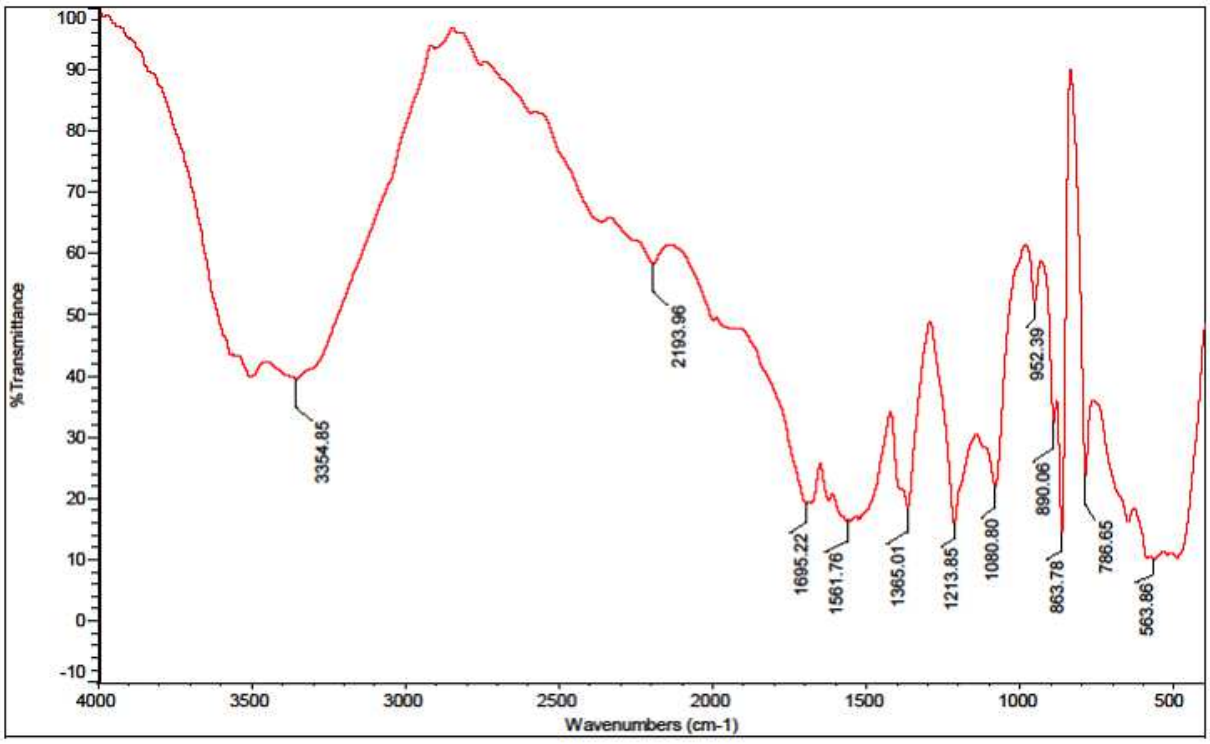


Fig.4.The FTIR spectrum of ASNMA crystal

The absorption peak at 3354.85cm^{-1} is due to the NH stretching of amino acid group and O-H group respectively. The peak at 2193.96 cm^{-1} is due to overtones and combination bands. The peak at 1695.22 is due to COO group attached with Na. The peak at 1213.85 were assigned to C-O-C asymmetric vibration due to the presence of conjugated C=C. The peak at 952.39 cm^{-1} is due to O-H out of plane bending, which conforms the presence of carboxylic acid group, and other characteristics vibrations of functional groups present in the compound are tabulated in Table.2.

Table.2.Band assignments of FTIR spectrum of ASNMA

Wave number (cm^{-1})	Assignments
3354.85	NH stretching
2193.96	Combination band
1695.22	COO^- Asymmetric stretching
1365.01	C-H deformation in CH_3
1213.85	C-O-C Asymmetric stretching
952.39	O-H out of plane bending
863.78	O-H out of plane deformation
786.65	O-C-O deformation
563.86	COO^- Wagging

3.3 UV-vis spectral analysis

UV-vis analysis gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electrons in π and σ orbitals from the ground state to higher energy states. The absorption spectrum of ASNMA crystal was recorded in the wavelength range of 200-2500nm in the entire near ultraviolet visible and near IR region using the carry 300 model. The waveleth ranges from 500 - 1500nm, the material is observed to be nearly transparent(the absorbance is less than 0.6).Absorption is observed between 1500 and 2500nm region which is due to overtones. From the spectrum(Fig.5) it is evident that ASNMA crystal has a very low cut off wavelength of 283nm,along with a large transmission window in the entire visible region. It is sufficiently low for SHG laser radiation at 1064 nm or other applications in the blue region.

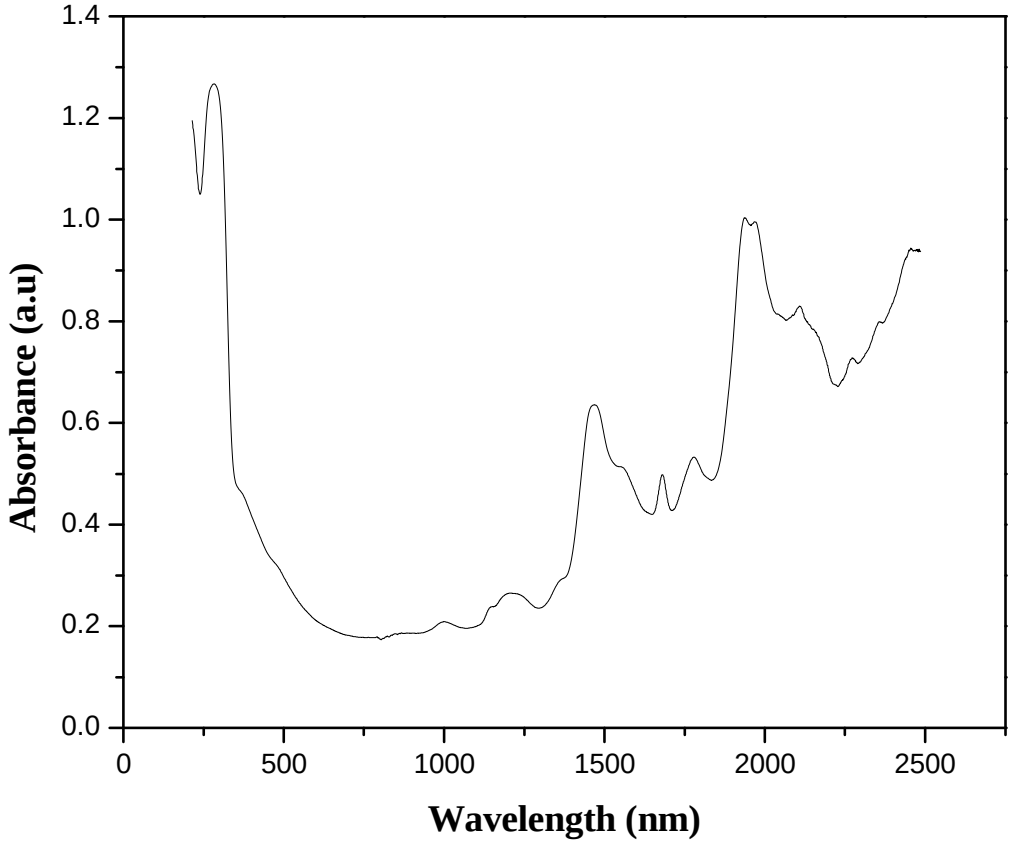


Fig.5.UV-Vis spectrum of ASNMA crystal

3.4 SHG studies:

The nonlinear optical conversion efficiency test was carried out for the grown crystals using the Kurtz and Perry technique. It is a popular method to evaluate conversion efficiency of a non linear optical material.KDP was used as a reference material for the present measurement. In this method, ASNMA crystals was powdered with a uniform particle size and then packed in a micro capillary tube. Thereafter the powder of ASNMA filled tube is exposed to laser radiation. Q-Switched Nd: YAG Laser emitting a fundamental wavelength of 1064 nm with pulse width 8ns was used. It was estimated that the conversion efficiency is1.3 times that of the standard KDP.

CONCLUSION

A new nonlinear optical semiorganic crystal, ASNMA, was grown by the slow evaporation technique from aqueous solution for the first time.. The study of cell parameters was calculated by single crystal X-ray diffraction analysis . The molecular structure of ASNMA crystal is presented in ORTEP diagram. Functional groups of good quality crystals of ASNMA have been detected by FTIR. The absorption spectra confirms that the ASNMA crystals are optically transparent and having low cutoff at 283 nm wavelength. The second harmonic generation efficiency measurement shows the grown ASNMA crystal having 1.3 times higher nonlinear optical efficiency than potassium dihydrogen phosphate (KDP).

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