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Low temperature redetermination of the Glycine sodium nitrate structure by using X-ray single crystal diffraction technique

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Abstract

The redetermined structure of glycine sodium nitrate, $C_2H_5N_2NaO_5$, at 150°K is reported. The compound has an overall polymeric structure whilst the glycine molecule is found in the zwitterionic form. GSN crystals were characterized by XRD powder diffraction, FTIR, UV-VIS, and DTA-TGA techniques. XRD revealed that GSN have a monoclinic structure and space group Cc. Infrared spectra confirmed that the chemical elements and functional groups are present in the crystals and also collaborated the zwitterionic form of molecule. Ultraviolet-Visible spectra showed a wide optical transparent window in the range of 340-1100 nm, which is a desirable characteristic for nonlinear optics applications. DTA-TGA analysis determined that the material is stable up to 198°C.

Keywords: Polymers; XRD; FTIR; UV-Vis.

Introduction

As part of research into materials for use in the field of nonlinear optics, crystals of glycine sodium nitrate (I) were prepared. Inorganic salts of amino acids have shown to be useful in nonlinear optics studies (Aggarwal, 2003; Rajan Babu, 2002; Razzetti, 2002). The room-temperature crystal structure of (I), refined in space group Cc, was reported by Krishnakumar et al. (2001) although no mention of the non-linear optical properties of the compound is discussed.



Experimental

Compound (I) was prepared by dissolving 32.83 g of glycine and 37.16 g of sodium nitrate in 100 ml of double-distilled water. Crystals were grown by slow solvent evaporation from a saturated solution over several weeks at a constant temperature of 30°C.

All H atoms were first located from a difference electron density map. N—H H atoms were freely refined. The C—H H atoms were refined as riding, with a C-H distance constrained to be 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2_{\text{eq}}(\text{C})$. Since the largest element in this structure is sodium, the value of the Flack parameter is meaningless due to lack of significant anomalous dispersion. Friedel pairs were thus merged during the final refinement.

Data collection: SMART (Bruker, 2001). Cell refinement: SAINT (Bruker, 2001). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 2001). Program(s) used to refine structure: SHELXTL. Molecular graphics: ORTEP3 forWindows (Farrugia, 1997). Software used to prepare material for publication: SHELXTL and local programs. Experimental detail appears as shown in Table I.

TABLE I.

Crystal data

$\text{C}_2\text{H}_5\text{N}_2\text{NaO}_5$	Mo $K\alpha$ radiation
$M_r = 160.07$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 1600 reflections
I_a	$\theta = 3.24 - 27.75^\circ$
$a = 9.140(6) \text{ \AA}$	$\mu = 0.226 \text{ mm}^{-1}$
$b = 5.294(4) \text{ \AA}$	$T = 150(2) \text{ K}$
$c = 12.747(9) \text{ \AA}$	Prism

$\beta = 99.765 (9)$	Colourless
$V = 607.8 (7) \text{ \AA}^3$	$0.21 \times 0.15 \times 0.15 \text{ mm}$
$Z = 4$	
$D_x = 1.749 \text{ Mg m}^{-3}$	
Dm not measured	
Data collection	
Bruker SMART 1K CCD 520 reflections with diffractometer	
Thin-slice ! scans	$I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.0227$
multi-scan SADABS;	$\theta_{max}/25.00 \triangleright \circ \circ \curvearrowright$
Sheldrick, 2006	
referenc	$h = -10 \text{ --- } 10$
$T_{min} = 0.9340,$	$k = -6 \text{ --- } 6$
$T_{max} = 0.9669$	
1993 measured reflec-	$l = -15 \text{ --- } 15$
tions	
539 independent reflec-	
tions	
Refinement	
Refinement on F2	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.1280P]$
$R[F^2 > 2\sigma(F^2)] = 0.0234$	Where $P = F_o^2 + 2F_c^2/3$
$wR(F^2) = 0.594$	$\Delta\rho_{max} = 0.000$
$S = 1.113$	$\Delta\rho_{max} = 0.140e \text{ \AA}^3$
539 reflections	$\Delta\rho_{min} = 0.177e \text{ \AA}^3$
103 parameters	Extinction correction: none
H atoms treated by a	Scattering factors from International
mixture of independent	Tables for Crystallography (Vol. C)
and constrained	
refinement	

Results and discussion

X ray powder diffraction

In order to confirm the crystalline structure of the synthesized material, powder diffraction data was taken in a X-PERT Philips diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.540598 \text{ \AA}$), using a step of 0.05° for the time interval of 10s, and a 2θ scanning between $10\text{-}60^\circ$. Figure 1 shows the diffraction pattern, the lattice parameters and the (hkl) planes. The plane reflections meet the experimentally reported structure which belongs to the monoclinic system space group Cc with cell parameters $a = 14.329 (3) \text{ \AA}$, $b = 5.2662 (11) \text{ \AA}$, $c = 9.1129 (18) \text{ \AA}$, $\beta = 119.10^\circ (3)$ and cell volume $V = 600.9 (2) \text{ \AA}^3$. The peaks in the XRD

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pattern were indexed, and differences in the positions of reflection of the planes with the diffraction pattern previously reported by Narayan Bhat N. and Dharmaprakash S.M. were observed.

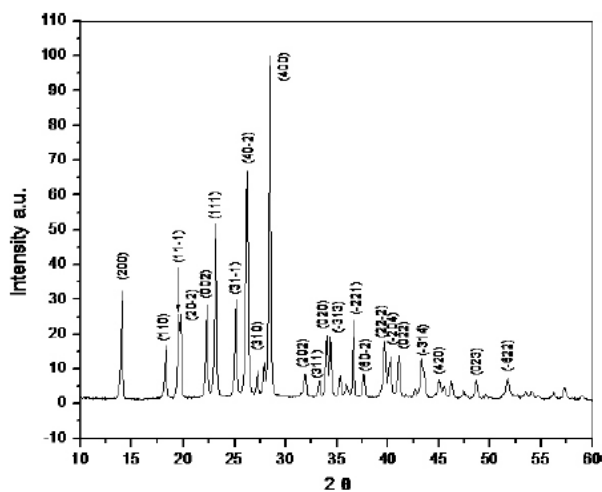


FIGURE 1. X-ray powder diffraction pattern of GSN.

FTIR studies

Functional groups present in the crystals were found using Fourier transform infrared (FT-IR) spectroscopy. The IR analysis was taken with a MAGNO IR 750 series II NICOLET spectrometer, within wave number range of 400-4000 cm^{-1} . The samples were added to a pellet of KBr.

Figure 2 shows the IR spectrum. Amino acids usually exist as a zwitterions form in crystals. They have an ionized carboxyl group (COO^-) and an amine salt (NH_3^+). The NH_3^+ stretching mode was found with broad band strength with multiple peaks between 3100-2600 cm^{-1} . This same mode can be seen at low frequencies up to 2200 cm^{-1} . At a 2036 cm^{-1} frequency, a primary amine resonant frequency is found and it is produced of a combination band of NH_3^+ asymmetric deformation and NH_3^+ rotation. A signal of

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1654cm^{-1} corresponds to NH_3^+ deformation and a 1511cm^{-1} corresponds to symmetric deformation.

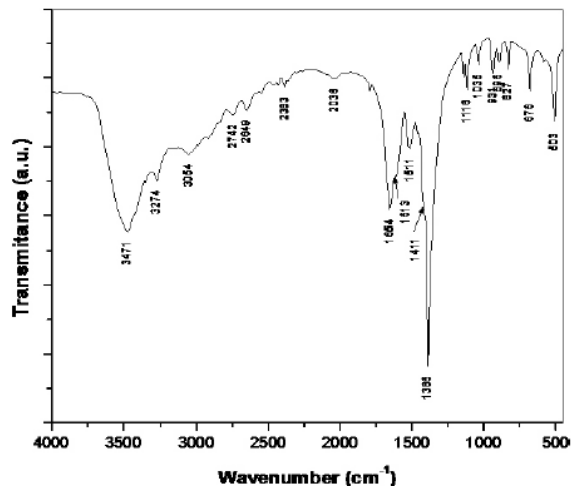


FIGURE 2. FTIR spectra of GSN crystals.

Two overlapped signals at 1613cm^{-1} and 1411cm^{-1} were attributed to asymmetric and symmetric stretch modes of the COO^- group. Other signals of deformation of the COO^- mode were shown at 676 , and at 503cm^{-1} . This confirms that the glycine molecule exists in a zwitterion form inside the crystal. The strongest absorption at 1386cm^{-1} is due to asymmetric NO_3 stretch and also appears at 827cm^{-1} as a weak signal. More variable bands were found matching amino acids.

UV-Vis spectroscopy

The UV-Visible characterization of GSN crystals was recorded with a lambda 10 Perkin Elmer UV-VIS spectrometer in the range of 1100-200 nm with a crystal thickness of 2.5 mm. Figure 3 shows the optical absorption of GSN. In this graph we could observe a practically straight line from the 1100 to 340 nm range that corresponds to the near infrared to the visible frequency of the electromagnetic spectrum; this is a

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desirable characteristic in NLO material, so there exist more efficiency of conversion of second harmonic generation (SHG).

Thermal analysis

GSN DTA-TGA analysis is shown in Fig. 4. The sample was analyzed in a TA Instruments STD 2960 using simultaneous DTA-TGA mode, and was heated at rate of 15°C/min in 50 cm³ of air. From DTA curve, it has been found that GSN is stable up to 198°C, because endothermic signals were not observed, which characterize crystalline transformations. From the 198°C to 226°C the material began to change phase until finally melted completely. TGA showed a loss of material at 226°C attributed to the decomposition of the organic part. At an elevated temperature this decomposition process continues up to 700°C. Also was observed that 2.4% of the water contained in the material, was lost before being fused.

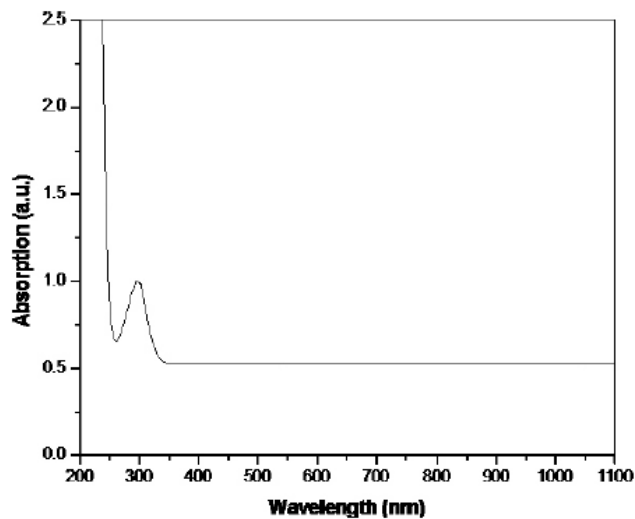


FIGURE 3. UV-Vis absorption spectra of GSN crystals.

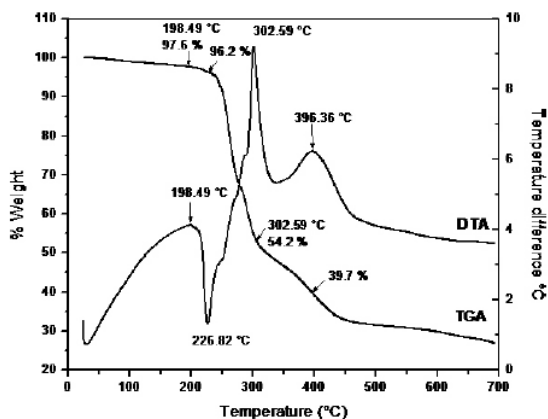


FIGURE 4. DTA-TGA curves of GSN.

Single crystal X-Ray diffraction

This low-temperature redetermination is presented in the conventional space group Ia. The asymmetric unit of (I) consists of one glycine molecule, one sodium cation and one nitrate anion. The structure is polymeric and the complete coordination environment of the sodium centre is shown in Fig. 5. The octa-coordinated sodium centre has essentially distorted hexagonal bipyramidal geometry, with apical glycine ligands. The bonding geometry is unexceptional. The glycine molecule exists as a zwitterion and N—HO hydrogen bonding secures the location of the N—H H atoms (Table II).

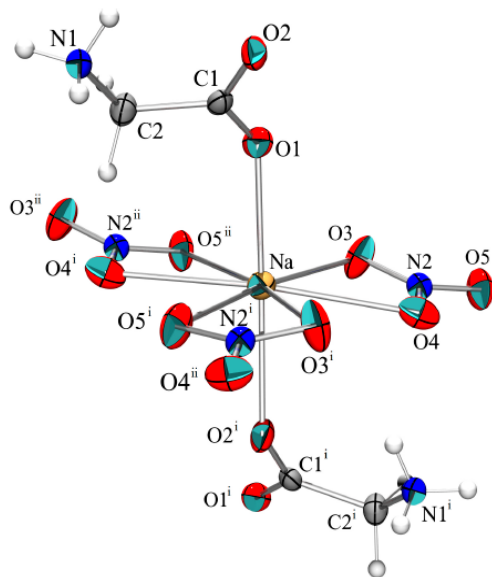


FIGURE 5. The complete coordination environment of the sodium centre in compound (I). Displacement ellipsoids are at the 50% probability level. Symmetry operators: (i), $x + 0, -y + 1/2, z 1/2$; (ii), $x - 1/2, -y, z$.

TABLE II. Hydrogen-bonding geometry ($\text{\AA}^\circ, ^\circ$)				
D—H...A	D—H	H—A	D—A	D—H—A
N1—H1N...O4i	0.87 (3)	2.32(3)	2.894(4)	124(2)
N1—H2N...O1ii	0.85 (4)	1.95 (4)	2.792 (3)	171 (4)
N1—H3N...O2iii	0.87 (5)	1.93 (5)	2.793 (4)	169 (4)

Symmetry codes: (i) x, \bar{y}, \bar{z} ; (ii) $x - \bar{y}, 1 - y, z$; (iii) $x, 1 + y, z$.

Conclusions

The constant temperature technique evaporation of the solution generated GSN crystals with a stable aminoacidionic salt combination, which was proven with XRD and FTIR analysis. We have proven that the existence of a dipolar molecule contributed to the formation of a noncentrosymmetric crystalline structure. Optical transmission studies showed that this material does not have electronic transitions in the range of 340 to 1100 nm and it may be used for SHG. Thermal analysis showed that GSN is stable up to 198°C, GSN crystals showed thermal stability and kept their crystalline structure.

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Finally we have been obtained the redetermination at low temperature of the GSN structure by swing the single crystal X- ray diffraction technique.

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