



Synthesis, growth and characterization of donor–acceptor π -conjugated N-chlorosuccinimide single crystals for nonlinear optical applications

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ABSTRACT

Single crystals of N-chlorosuccinimide (NCS) were grown by slow evaporation solution growth technique. The grown crystals were confirmed by single crystal X-ray diffraction and FT-IR studies. The theoretical factorial group analysis was carried and the vibrational modes are assigned. The dielectric behaviour studied both as function of frequency and temperature reveal that, as frequency decreases more and more charge accumulation occurs at the interface between electrode and electrolyte, which leads to a drop in conductivity at low frequencies. The first order hyperpolarizability value determined by quantum chemical calculations are well supported by the results obtained from Kurtz–Perry powder technique.

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1. Introduction

Organic crystals for quadratic nonlinear optics have been intensely studied during the past 25 years. The research for large quadratic susceptibilities $\chi(2)$ depending on the quasi perfect packing of highly polarizable molecules in the crystal network has been the main challenge [1]. These molecules with π conjugated electronic structures have been attracting considerable interest due to their potential nonlinear optical (NLO) properties and applications in optoelectronic and photonic devices [2]. The advantages of organic materials are: (1) they are generally cheap to synthesize; (2) they can be conveniently purified by conventional techniques; (3) they have low dielectric constants; (4) provided that the crystals are pure, they will be striation free since compositional vibrations cannot occur [3]. The diverse properties of organic compounds are largely due to the unsurpassed ability of the carbon atom to form a variety of stable hybridized bonds with itself and many other elements. The average organic molecule may contain dozens of σ and π bonds. It is the π electrons that differentiate organic NLO materials from inorganic systems in which a few such conjugated counterparts exist. Unlike the electrons in the σ bonds, the electron density of a π bond or a series of π bonds is much more mobile [4]. Virtually all organic NLO molecules contain π bonds such as

single short polar π bond of the carbonyl as in urea or a more extended series of π bonds as in benzene and substituted benzene derivatives.

N-chlorosuccinimide (NCS) is a chlorinating and oxidizing agent which is used as a source for chlorine in radical reactions and various electrophilic additions. This crystallizes in the orthorhombic crystal system [4]. NCS contains a five-member ring and two $\text{C}=\text{O}$ double bonds. The molecular structure is shown in Fig. 1. This paper deals with the synthesis, growth and characterization of NCS single crystals.

2. Experimental

2.1. Material synthesis

Salt of NCS was synthesized by dissolving 160 g of succinimide in a mixture of 64 g of NaOH, 300 g of crushed ice and 400 ml of deionized water. The mixture was cooled in an ice bath, and 85 ml (1.65 mol, 264 g) of Cl_2 was added. The solution was continuously stirred during the process. The resultant solution was refluxed for 2 h and the precipitate product was filtered and washed with ice water. The synthesized NCS was dissolved in deionized water at 100 °C in 125 ml of deionized water for every 10 g of NCS in an Erlenmeyer flask. The crystalline materials of NCS were collected by vacuum filtration over a bed of ice and were dried in air. It is to be noted here that the chlorine was nonreactive below the temperature of 100 °C. The synthe-

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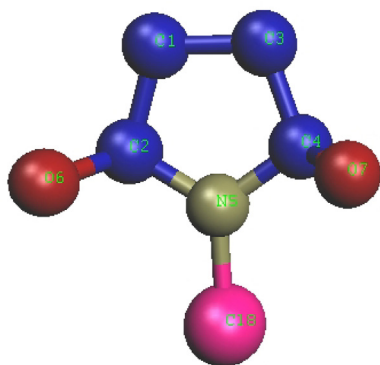


Fig. 1. Molecular structure of NCS.

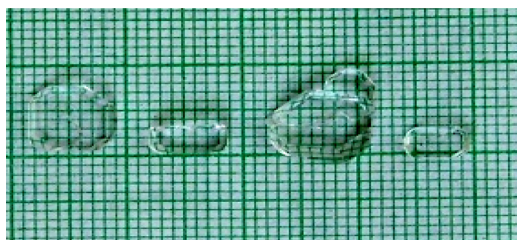


Fig. 2. As grown NCS single crystals.

sized NCS was confirmed by Fourier transform infra red (FT-IR) analysis.

2.2. Crystal growth

Growth of organic crystals having well-developed faces and good quality mainly depends on the choice of suitable solvents. Solvents offering moderate solubility–temperature gradient for a material and yielding prismatic growth habit will be considered as suitable solvent for growing crystals of that material. Hence the solubility of NCS in various solvents like methanol, ethanol and benzene was analyzed and it was inferred that the title compound exhibits good solubility and a positive solubility temperature gradient (direct solubility) in benzene. Single crystals of NCS have been grown from saturated solution of the synthesized salt of NCS by the slow evaporation solution growth technique at 40 °C using a constant temperature bath having a control accuracy of (± 0.01 °C). Transparent pyramidal crystals were harvested after a growth period of 30–40 days. The as grown NCS single crystals are shown in Fig. 2.

3. Characterization studies

3.1. Single crystal X-ray diffraction studies

Single crystal X-ray diffraction study was carried out on the as grown NCS crystal using ENRAF NONIUS CAD4 single crystal X-ray diffractometer. From the XRD analysis it is confirmed that the as grown NCS crystal belongs to the orthorhombic crystal system with $P2_12_12_1$ space group. The obtained crystallographic data are in good agreement with the values reported in the literature [5] and the values are presented in Table 1.

3.2. Spectral analysis

3.2.1. Factor group analysis

Factor group analysis provides a basis for the prediction of lattice vibrations and the vibrational spectral studies provide information

about the charge transfer interaction between the donor and acceptor groups through π -electron movement. The procedure outlined by Rosseau et al. [6] was followed to carry out the factor group analysis.

As NCS crystallizes in the orthorhombic crystal system with the non-centrosymmetric space group $P2_12_12_1$ (D_2^4) the Bravais cell consists of 4 molecules and occupy the general sites of $C_1(4)$ symmetry. A single molecule of NCS contains 12 atoms which in turn gives rise to (12×4) 48 atoms in a unit cell. The representation Γ_{total} , of all the vibrations can be decomposed according to the irreducible representation of the point group $C_1(4)$ as $[36A + 36B_1 + 36B_2 + 36B_3]$ which includes the three acoustic modes corresponding to the block translations of the crystal $\Gamma_{\text{vib, acoustic}} = B_1 + B_2 + B_3$.

3.2.1.1. Analysis of vibrational spectra. The vibrational analysis reveals the structure of the co-ordinated compound and the confirmation of the material. The formal classification of fundamental mode predicts that the 120 internal vibrations can be distributed as $(30A + 30B_1 + 30B_2 + 30B_3)$ and 24 external modes such as $(3A + 3B_1 + 3B_2 + 3B_3)$ translational and $(3A + 3B_1 + 3B_2 + 3B_3)$ rotational vibrational modes. The theoretical vibrations of NCS may be due to the lattice and internal vibrations of the co-ordinated compounds and mostly due to the CH_2 and CN groups. The bands observed from 500 to 4000 cm^{-1} are due to the internal vibrations of the co-ordinated compounds and below 500 cm^{-1} are due to the deformational, translational and rotational vibrations. Phonons belonging to B_1, B_2 and B_3 are both Raman and infrared active. However the phonons belonging to A symmetry are Raman active and IR inactive. The factor group analysis and summary are presented in Tables 2 and 3 respectively.

3.2.1.2. Internal vibrations. NCS molecule does not have any symmetry and so the internal vibrations exhibited are of both IR and Raman active exclusive of acoustic mode. The internal vibrations may be classified as those arising from the CH_2 , CN , CO and N-Cl functional groups. These vibrations are strongly coupled between themselves.

3.2.1.3. External vibrations. The external vibrations are mainly due to the bands observed below 500 cm^{-1} owing to the rotational and translational modes of vibrations of NCS ions. The rotational modes are expected to have higher frequency and intensity than translational modes in the Raman spectra. However the translational modes are more intense in IR spectra. There are 24 external modes and these vibrations can be achieved experimentally by polarized

Table 1

Comparison of single crystal X-ray data of NCS crystal.

Parameter	Observed value (Å)	Reported value (Å) [5]
<i>a</i>	6.410	6.412
<i>b</i>	7.121	7.111
<i>c</i>	11.690	11.691

Table 2

Results of factor group analysis of NCS.

Sl. no	Factor group symmetry (D_4^2)	A	B_1	B_2	B_3
1	External modes	6	6	6	6
	(i) Translational	3	3	3	3
	(ii) Rotational	3	3	3	3
2	Internal modes	30	30	30	30
	Total	36	36	36	36

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