

Spectral, Structural, Thermal and Optical Characterisation of A New Organic D- π -A type Material: m-nitroanilinium L-tartrate m-nitroaniline

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A new organic SHG active salt 3-Nitroanilinium L-tartrate m-nitroaniline (MLM) was synthesized and optically good single crystals were grown by solvent evaporation solution growth method at room temperature. The structure of the crystal identified by single crystal XRD analyses and it belongs to monoclinic crystal system with polar space group P2₁. The functional groups present in product have been confirmed from the FT-IR spectral study. The optical transmission spectrum was recorded to examine the optical property of the title crystal. The thermo gravimetric and differential thermal analyses were carried out simultaneously to study the thermal behavior of the title crystal. The relative second harmonic generation activity of the title crystal was confirmed by the modified Kurtz-Perry powder test and it was found that the title crystal has 0.5 times second harmonic generation output than that of KDP.

Introduction

A great deal of work has been devoted to the construction and designing of potential nonlinear optical materials owing to their potential applications in frequency conversion, optical parametric oscillation, high-speed information processing, and storage, optical switching and telecommunication [1-4]. Among the various nonlinear optical materials organic nonlinear optical materials possess unique properties like higher nonlinear coefficient, high laser damage thresholds, wide optical transparency window in addition to that large single crystals can be grown by slow solvent evaporation technique at room temperature [5, 6]. The augmented charge transfer activity due to the intermolecular hydrogen bonding in turn favours asymmetric polarization and increase the SHG efficiency of the compound [7-9]. Hydrogen bonding interactions not only facilitates the SHG activity but also improves the mechanical and thermal stability of the crystal [10, 11]. 3-nitro aniline and L-tartaric acid both are well known organic nlo materials. L-tartaric acid due to its molecular chirality it ensures noncentrosymmetric crystalline packing in most of its compounds. This aspect fulfils the prime requirement for SHG activity of the material and hence variety of tartrate crystals shown to possess SHG activity [12-15].

Experimental

Synthesis and crystal growth

MLM was synthesized by mixing equimolar methanolic solutions of 3-nitroaniline and L-tartaric acid and the solution was mixed well for homogeneous condition, then

the solution was filtered to remove the insoluble products and kept in a dust free stable place for evaporation, after the ten days' time the crystalline yellow precipitate of the 3-nitroanilinium L-tartrate (MLM) was obtained. The product was filtered off dried and single crystals of MLM have been grown from the saturated methanolic solution by solution growth technique. The photograph of the grown crystals shown in Fig. 1.

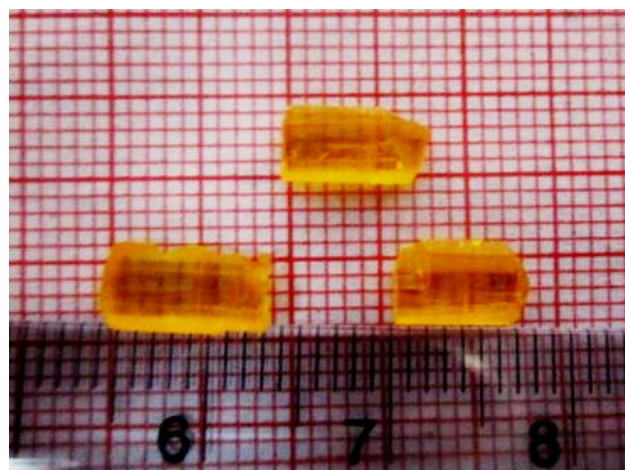


Fig. 1. As-grown crystals of MLM.

Characterization

The nature of the crystal, the packing of asymmetric units in the three dimensional space was determined from the single crystal X-ray diffraction analysis obtained with a Bruker Kappa Apex-II diffractometer (Graphite monochromated, MoK α = 0.713). Infra-red spectrum of

the title compound was recorded using potassium bromide pellet method employing a Perkin Elmer FT-IR spectrometer in the range 4000-450 cm^{-1} . The UV-Vis-NIR transmittance spectrum was recorded employing Varian Cary 5E UV-Vis-NIR spectrophotometer. The TGA and DTA thermal studies were carried out on a S-II Nanotechnology TG/DTA 6200 instrument at a heating rate of 20°C/min. Quantitative estimation of relative SHG efficiency of NALT crystal with reference to KDP was done by modified Kurtz-Perry powder test using a Nd:YAG laser (1064 nm).

Results and discussion

Single crystal XRD analysis

The obtained XRD data shows that MLM belongs to the crystal system with polar space group $P2_1$, and the cell parameters $a = 7.2402(5) \text{ \AA}$, $b = 11.9042(6) \text{ \AA}$, $c = 10.6809(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.879(2)^\circ$, $\gamma = 90^\circ$. The crystal data and details of the data collection and the structure refinement of the structure are given in **Table 1**. The asymmetric unit of MLM contains one protonated 3-nitroanilinium cation, one tartrate anion and a neutral 3-nitroaniline molecule these three asymmetric units combined together through various intermolecular hydrogen bonds of both O-H-O and N-H-O type.

Table 1. X-ray diffraction refinement of MLM.

Empirical formula	$\text{C}_{16} \text{H}_{18} \text{N}_4 \text{O}_{10}$
Formula weight	426.34
Temperature	296(2) K
Wavelength	0.71073 \AA
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimensions	$a = 7.2402(5) \text{ \AA}$ $\alpha = 90^\circ$ $b = 11.9042(6) \text{ \AA}$ $\beta = 91.879(2)^\circ$ $c = 10.6809(6) \text{ \AA}$ $\gamma = 90^\circ$
Volume	$920.08(9) \text{ \AA}^3$
Z, Calculated density	2, 1.539 Mg/m^3
Absorption coefficient (000)	0.130 mm^{-1} 444
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	3.29 to 28.26 $^\circ$
Limiting indices	$-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $-13 \leq l \leq 14$
Reflections collected / unique	6832 / 4343 [R(int) = 0.0160]
Completeness to theta =	28.26 98.5 %
Max. and min. transmission	0.9744 and 0.9498
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4343 / 3 / 288
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0339$, $wR_2 = 0.0872$
R indices (all data)	$R_1 = 0.0384$, $wR_2 = 0.0904$
Absolute structure parameter	1.0(7)
Largest diff. peak and hole	0.207 and $-0.159 \text{ e. \AA}^{-3}$

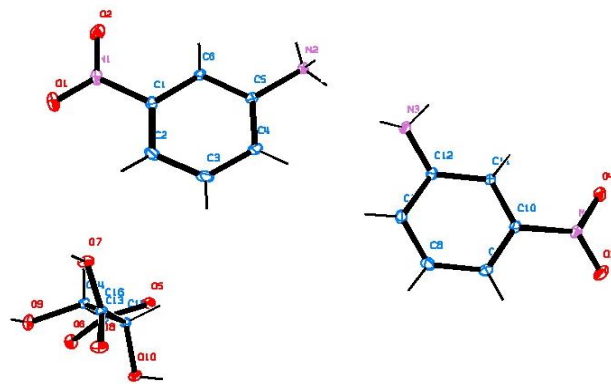


Fig. 2. Ortep view of MLM crystal.

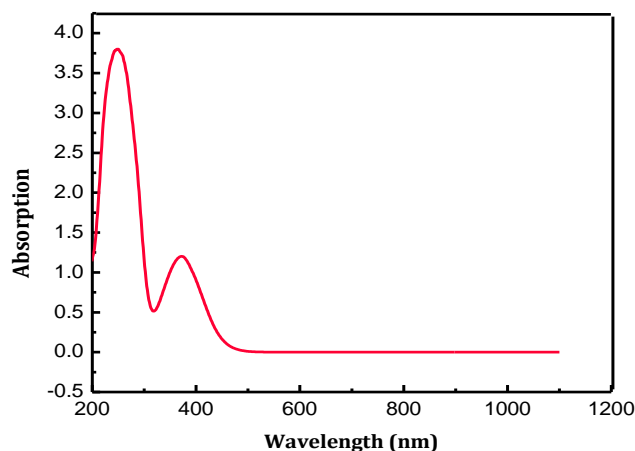


Fig. 3. UV-Vis absorption spectrum of MLM.

UV-Vis-NIR spectral studies

The recorded UV-Visible absorption spectrum of MLM crystal is shown in **Fig. 3** from the spectrum it is observed that the spectrum exhibits the characteristic absorption band due to the charge transfer transition along with the usual $\pi-\pi^*$ of 3-nitroaniline and L-tartaric acid moieties of the charge transfer complex salt. This charge transfer band arises due to the transfer of an electron from donor L-tartaric acid molecule to the acceptor m-nitroaniline molecule and appears on the longer wavelength side of the spectrum at 398 nm. This band confirms the presence of intermolecular charge transfer activity in MLM salt. The usual $\pi-\pi^*$ band of 3-nitroanilinium moiety of the Title salt appear at 250 nm. The crystal also has a wide transparency window in the visible and NIR regions upto 1200 nm.

FT-IR spectral studies

The formation of the title salt is confirmed by the FT-IR spectral study and the spectrum shown in **Fig. 4**. The broad vibration band appears at 3430 cm^{-1} is attributed to the hydrogen bonded O-H stretching vibration of L-tartrate moiety. The band observed at 3321 cm^{-1} is attributed to the aromatic N-H stretching vibration of 3-nitroaniline moiety which is present as a neutral third partner in the asymmetric unit. The absorption band

at 3090 cm^{-1} corresponds to the aromatic $\text{N}^+ - \text{H}$ stretching vibration of 3-nitroanilinium moiety. The C-H stretching vibration of methine group is observed at 2869 cm^{-1} . Associated O-H stretching vibration of carboxyl group in l-tartrate moiety appears at 2538 cm^{-1} . The C=O stretching vibration of L-tartrate moiety in the MLM complex salt is observed at 1722 cm^{-1} . The asymmetric and symmetric COO^- stretching vibrations of L-tartrate moiety in the salt are observed at 1620 and 1405 cm^{-1} respectively. The characteristic asymmetric and symmetric NO_2 stretching vibration bands appear at 1521 and 1343 cm^{-1} respectively. The vibration bands observed below 500 cm^{-1} are due to the skeletal vibrations.

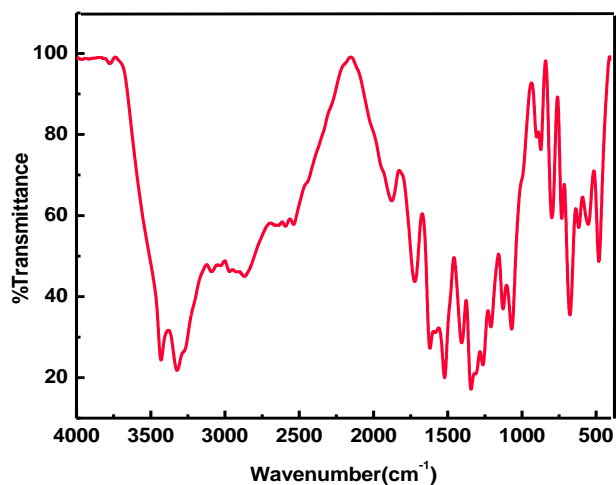


Fig. 4. FT-IR spectrum of MLM.

Thermal analyses

The thermal stability of MLM crystal has studied by using thermo gravimetric and differential thermal analysis techniques. The DTA supports the same changes shown by TGA. From the TG thermogram it is understood that the substance is stable upto 164°C and it melts immediately after melting. The decomposition occurs in three stages. This is further confirmed by DTA. The endothermic dip at 164 °C corresponds to the melting point of the substance after which the compound decomposes immediately into various volatile gaseous molecules like NO_2 , CO_2 and a mixture of hydrocarbon gases. As has been evident from the TG, DTA thermogram the substance undergoes total decomposition around 500°C into various gaseous products like NO_2 , CO_2 and a mixture of hydrocarbon gases.

Second harmonic generation efficiency

The second harmonic generation output has been identified using the modified experimental setup of Kurtz and Perry. The nonlinear optical activity of the title salt was confirmed by the emission of green light. The SHG conversion efficiency of MLM is found to be about 0.5 times that of standard KDP with a similar grain size. The SHG output of the title salt might be attributed to the head to tail arrangement of 3-nitroanilinium cation by the

L-tartrate anion and the D- π -A type charge-transfer interaction by the intermolecular hydrogen bonds between the 3-nitroanilinium cations and L-tartrate anions [16].

Summary

A new organic D- π -A SHG active hydrogen bonded salt MLM was synthesized and good quality single crystals were grown by solution growth technique at room temperature. The recorded FT-IR spectrum confirms the presence of various functional groups as well as existence of intermolecular hydrogen bonding between the constituent species. The optical transmittance spectrum substantiates the suitability of the title crystal for various optical applications. The thermal stability of the title salt was established by TG/DTA studies and shown that the title compound thermally stable upto 164°C. The relative SHG efficiency of MLM was shown to be 0.5 times that of the standard reference KDP.

Supplementary material

CCDC 946243 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336033.

Keywords

Organic compounds, optical materials, crystal growth, infrared spectroscopy, crystal structure.

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