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Investigations on the new organic NLO single crystal: Thiourea Mono Acetate (TMA)

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ABSTRACT

The organic nonlinear optical (NLO) crystals of thiourea mono acetate were grown by slow evaporation method. The solubility study was carried out for water solvent from 30 to 50 °C. Powder XRD study reveals the crystalline nature of the grown sample. The mode of vibration of different molecular groups present in TMA was identified by FTIR spectral analysis. The UV-vis-NIR spectrum of TMA shows less optical absorption and good transmittance in the entire visible region. The second harmonic generation (SHG) was confirmed by Kurtz powder method. The frequency dependent dielectric studies were carried out. The dielectric constant and dielectric loss of TMA were measured in the frequency range 100 Hz to 5M Hz at different temperatures. The photo current and dark current with applied field were measured. The grown crystal of TMA exhibit negative photoconductivity and reported for the first time.

Introduction

Nonlinear optical materials have been attraction a great deal of interest due to their applications, like high speed information processing, optical communications, optoelectronic and optical data storage [1-4]. As NLO materials, organic materials attract lot of interest from chemists, materials scientists, and optical physicists because of their superior performance with respect to NLO properties, such as the large NLO co-efficient, ultra nonlinear response time and high optical damage threshold [5-9]. The nonlinear optical properties of some of the thiourea based organic crystals such as, dye doped thiourea crystals, glycine thiourea crystals, urea thiourea mixed crystals [10-13]. The microscopic origin of nonlinearity in the organic molecular NLO materials is due to the presence of delocalized π electron systems connecting donor and acceptor groups, which enhance the necessary asymmetric polariability [14]. The donor and acceptor groups provide the ground-state charge asymmetry of the molecule, which is required for second order nonlinearity. Due to the bulk NLO properties are dependent on the first-order hyperpolarizabilities of molecules, NLO properties of molecules and their hyperpolarizabilities have become an important area of extensive research [15-20]. Therefore, in the present paper the synthesis, crystal growth, and experimental characterization of TMA crystal are fully reported for the time.

Experimental procedure

Synthesis

Thiourea mono acetate has been synthesized by dissolving AR grade of thiourea (99-100 %) and acetic acid (99.8%) in the equimolar ratio in (1:1) at room temperature. Thiourea mono acetate crystal was synthesized according to the following reaction. The molecular structure of TMA is shown in figure 1.

$CH_4N_2S + C_2H_4O_2 \text{ --> } CH_3COO^- N^+H_3CSNH_2$

Thiourea + Aceticacid ----> thiourea mono acetate

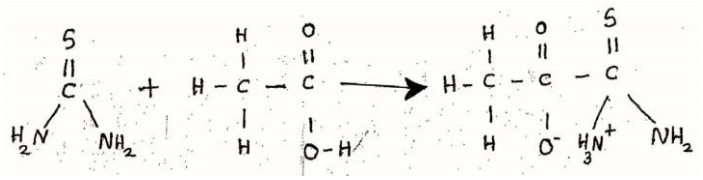

Fig 1. Molecular structure of thiourea mono acetate (TMA) crystal

Solubility Study

The growth rate of a crystal depends on its solubility and temperature. Since the solvent and solubility factors define supersaturation , which is the driving force for the rate of crystal growth. The synthesized salt of thiourea mono acetate (TMA) was used to carry out the solubility studies for the particular solvent. The solubility of TMA in double distilled water solvent was determined for various temperatures from 30 - 50 °C in the 5 °C intervals. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically [21]. The solubility curve for TMA is shown in figure 2. The solubility curve of the compound shows that the solubility increases linearly with temperatures.

Growth of TMA crystal

In order to improve the purity, the synthesized salt of thiourea mono acetate was purified by successive recrystallization process for two times. Then the synthesized salt was used to grow a crystal of thiourea mono acetate. By adopting the slow evaporation technique, the thiourea mono acetate seed crystals were obtained in the period of 7-10 days. The bulk size of the grown crystal was 7×6×2 mm^3 harvested in the period of 20 to 30 days. The grown crystals have no inclusion, defect free and good transparent in nature. As grown crystals of thoiurea mono acetate are shown in the figure 3.

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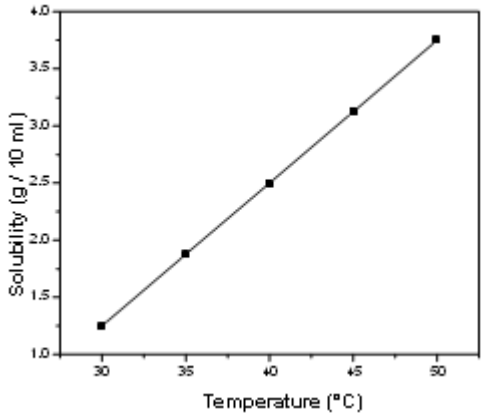

Fig 2. Solubility curve of thiourea mono acetate

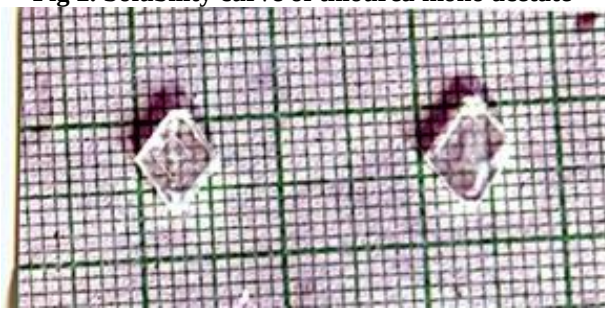

Fig 3. Photograph of as grown crystals of thiourea mono acetate

Characterization

The grown crystals have been analyzed by different characterization techniques. The crystalline nature of TMA was confirmed by powder X-ray diffraction analysis using BRUKER, Germany (model D8 Advance) X-ray diffractometer. Also the formation and quality of compounds were checked by x-ray powder diffraction (PXRD) spectrum. The functional groups were identified by using BRUKER Fourier Transform infrared spectrometer in the range of 400-4000 cm^{-1}. The optical absorption spectrum of TMA crystal was taken in the wavelength range 100 – 1000 nm by Varian Cary 5E model spectrophotometer. A Q-switched mode locked Nd:YAG laser, used to generate about 6.2 mJ/pulse at the 1064 nm fundamental radiation, was used for SHG efficiency measurements. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in Between two transparent glass slide. The grain size of the sample in general varied between 98 and 120 nm. The light emitted by the sample was measured using the photodiode detector and oscilloscope assembly. The dielectric constant and dielectric loss was carried out by using HIOCKI model 3532 – 50 LCR HITESTER. The photoconductivity nature of the grown sample was investigated by PICO AMMETER (Keithley 485).

Powder x- ray diffraction (PXRD) analysis

The powder samples have been analyzed by using BRUCKER, Germany (model D8 Advance) X-ray diffractometer with cuk_{alpha} (wavelength=1.5405 A°) radiation. The powder X-ray diffraction pattern of thiourea mono acetate crystal is shown in the figure 4. The well defined Bragg peaks are obtained at specific 2θ angles. The powder sample was scanned over the range 10 – 80° at a scan rate of 1° / min. The well defined peaks are reveals that the grown crystal has good quality and high crystalline nature. The observed d–values for different 2θ and full width half maximum (FWHM) for the crystal are given in the table 1. The crystalline particle size (D) is calculated by using the Scherer's formula from the full width half maximum value (FWHM),

$$D = [K \lambda / \beta \cos \theta]$$

Where, β is the broadening of diffraction line measured at half of its maximum intensity in radians, λ is the x-ray wavelength (λ = 1.54098 A^{o}), k is a constant taken as 0 .94 & θ is the Bragg's angle. The calculated average crystallite size is about 98.52 nm.

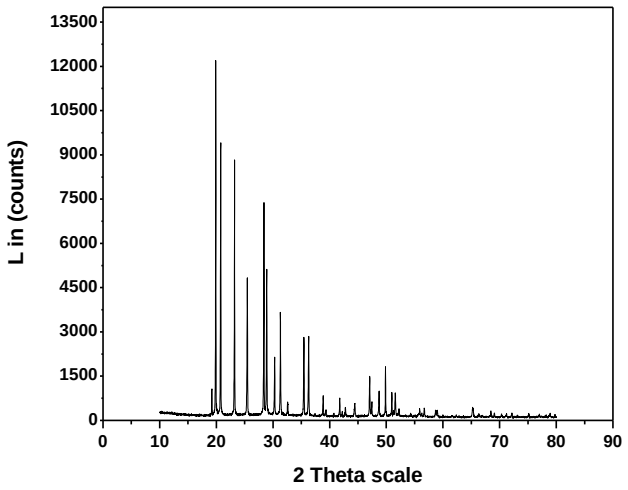

Fig 4. X-ray powder diffraction pattern of TMA crystal

Table 1. Measurement of the Size of TMA by using Debye-Scherrer's equation

No.	2θ (Deg)	FWHM	β =(3.14/180)* FWHM	cos θ	D = K λ / β .cosθ (nm)
1	19.204	0.082	0.001431	0.9887	102.35
2	19.900	0.075	0.001309	0.9878	112.00
3	20.358	0.086	0.001501	0.9873	97.72
4	23.203	0.069	0.001204	0.9834	122.31
5	25.467	0.102	0.001779	0.9801	83.05
6	28.281	0.079	0.001379	0.9755	107.65
7	30.270	0.110	0.001919	0.9719	77.64
8	31.311	0.097	0.001692	0.9699	88.25
9	32.583	0.093	0.001622	0.9675	92.28
10	35.455	0.097	0.001692	0.9615	89.02
11	36.710	0.096	0.001675	0.9587	90.18
12	49.703	0.091	0.oo1587	0.9248	98.67
13	49.865	0.075	0.001309	0.9244	119.68

Fourier Transform Infrared (FTIR) Spectral Analysis

The infrared spectral analysis is effectively used to understand the chemical bonding and it provides information about molecular structure and various functional groups of the synthesized compound. The FTIR spectrum was recorded using BRUKER FTIR Spectrometer by KBr pellet mehod in the range 400 - 4000 cm^{-1}. The FTIR spectrum of grown crystal is shown in the figure 5. The observed bands along with their vibrational assignments have been tabulated in table 2. Here the characteristics vibrational absorption of TMA crystal has been compared with acetic acid and thiourea. In the high energy region there is a broad band obtained between 3382 to 1615 cm^{-1}. It includes that the absorption observed for TMA at 3382.89, 3278 and 1814 cm^{-1} in the spectrum which corresponds to the 3376, 3280 and 1819 cm^{-1} absorption of thiourea [22, 23]. These absorption peaks can be assigned to NH_2 asymmetric stretching, NH_2 bending and N-H stretching modes of vibrations. The C-H and C=O stretching peaks observed at 2681.06 and 1615.78 cm^{-1} respectively in the spectrum of TMA compared with

absorption peaks of acetic acid at 2684 and 1617 cm^{-1} are clearly shows that the presence of acetic acid in the synthesized compound [24]. The sharp absorption peaks observed at 1467.13 , 1081.65 and 728.06 cm^{-1} in the spectrum of TMA corresponds to the 1472, 1083 and 730 cm^{-1} absorption of thiourea can be assigned to C-N asymmetric stretching , N-C-N symmetric stretching and C=S symmetric bending vibrations respectively [25, 26].

The absorption peaks of TMA at 1411.63, 628.46 and 480.74 cm^{-1} are clearly shows that absorption peaks of acetic acid.

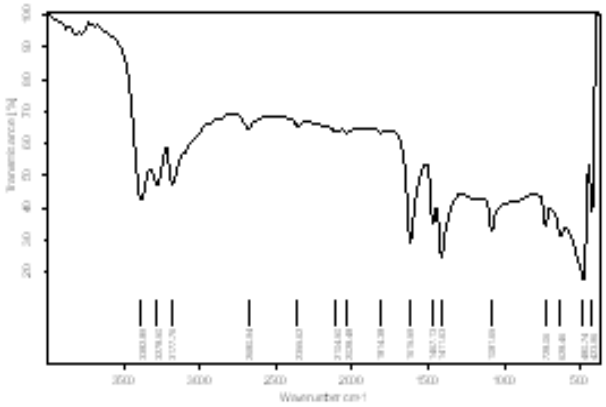

Fig 5. FTIR spectrum of Thiourea mono Acetate (TMA) crystal

Table 2. Vibrational assignment of TMA crystal

Thiourea mono acetate (TMA)	Wavenumber (Cm^{-1})		Assignment
	acetic acid	thiourea	
3382.89	-	3376.00	NH_2 asymmetric stretching
3278.50	-	3280.00	NH_2 bending
2680.94	2684.00	-	C-H stretching
1814.38	-	1819.00	N-H stretching
1615.59	1617	-	C=O stretching
1467.13	-	1472.00	C-N asymmetric stretching
1411.63	1414.00	-	Finger print region
1081.65	-	1083.00	N-C-Nsymmetric stretching
728.06	-	730.00	C=S symmetric bending

Optical Absorption Study

The optical absorption spectrum of TMA crystal recorded in the wavelength range from 200 to 900 nm is shown in the figure 6. Optically polished single crystal of thickness 2 mm was used for this study. The recorded spectrum gives limited introduction about the structure of the molecule, because the absorption of UV and visible light involves promotion of the electron in the σ and π orbital from ground state to higher energy state. From the absorption spectrum, it is clearly seen that the absorption is minimum in the entire visible region for grown crystal of TMA. However, the lower cut-off wavelength of TMA crystal is found to be around 240 nm. The crystal has transparent from 240 to 900 nm. Hence it is concluded that the grown crystal is very useful for optical applications in this range [27] . The optical band gap energy of the grown crystal was calculated using the formula, E_g = [1240/ λ (nm)] in eV. Where, λ is the lower cut off wavelength in (nm). The band gap of the TMA crystal is found to be 5.17 eV.

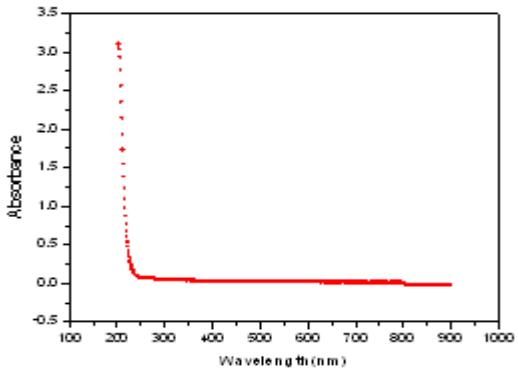

Fig 6. UV- vis- NIR spectrum of TMA crystal

NLO Studies

In order to confirm the NLO property, powdered samples were subjected to KURTZ and PERRY technique which remains powerful tool for initial screening of materials for SHG [28]. The beam of wavelength (λ =1064 nm) from Q-switched Nd:YAG laser was [Quanta ray series] supplied by spectra physics, USA and coherent Molectron power meter, USA made to fall normally on the prepared powdered sample, which was packed between two transparent glass slide. The SHG behavior was confirmed by the emission of bright green radiation (532 nm) from the sample. The measured amplitude of second harmonic generation for TMA crystal is 8.4 mJ and 8.8 mJ for KDP crystal. It shows a powder SHG efficiency of TMA crystal is about 0.9 times of KDP. The good second harmonic generation efficiency indicates that the TMA crystals can be used for application in nonlinear optical devices.

Dielectric Studies

Suitably cut and polished section of TMA crystal was subjected to dielectric studies using a HIOCKI model 3532-50 LCR HITESTER instrument. The measurements were made on the sample by varying the frequency from 100 Hz to 5 MHz at five different temperatures. Figure 7 shows the variation of dielectric constant of TMA crystal as a function of frequency. It is found that the dielectric constant of TMA is high at low frequencies and it decreases with increasing frequency which may be the space charge polarization contributes to the dielectric constant at low frequency [29]. Figure 7 shows that normal dielectric behavior of the sample, the dielectric constant decreases with increasing frequency and reaches a constant value, depending on the fact that beyond a certain frequency of the electric field, the dipole are not responding and follow the alternating field. The dielectric loss is also studied as a function of frequency for different temperature is shown in the figure 8. These curves suggest that the dielectric loss strongly depends on the frequency of the applied, similar to what commonly happens with the dielectric constant in the ionic system. [30]. The dielectric loss is high at low temperature and decrease with increase in frequency.

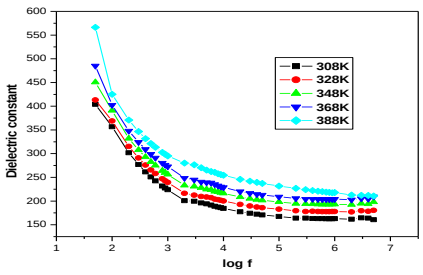

Fig 7. Variation of dielectric constant with log frequency for TMA crystal

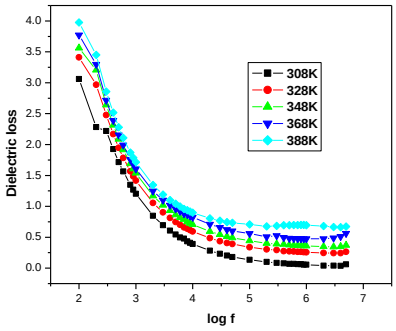

Fig 8. Variation of dielectric loss with log frequency for TMA crystal

Photoconductivity Studies

Field dependent photoconductivity study of TMA was carried out using Keithley 485 pico ammeter. The applied field was increased from 100 to 3830V/cm and the corresponding dark current was recorded. For the same set of applied field, the sample was then exposed to the radiation from a 100 W halogen lamp and the photocurrent was measured. Figure 9 shows the variation of both dark and photo currents with applied field. The plot reveals that both the dark and photo current increase linearly with the applied field , but photo current is found to be less than that of the dark current indicating the 'negative photoconductive' nature of TMA. The negative photoconductivity exhibited by the sample may be due to the reduction in the number of charge carriers in the presence of radiation. [31, 32].

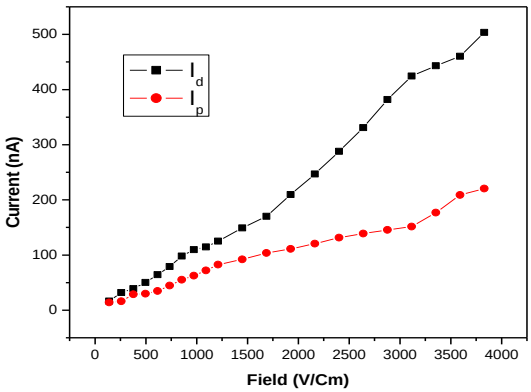

Fig 9. Field dependent photoconductivity of TMA crystal

Conclusion

Thiourea mono acetate single crystals have been grown from aqueous solution by slow evaporation method. The quality of crystal and crystalline nature was determined by using X-ray powder diffraction analysis. The Various functional groups are presented in the crystal have been confirmed by the FTIR analysis. The UV-Vis absorption spectrum reveals that the TMA has lower cutoff wavelength around 240 nm and show minimum absorption in the range of 240- 940 nm. From the optical absorption study, the band gap energy for the grown crystal (TMA) was found to be 5.17 ev. The SHG efficiency of the TMA crystal has 0.9 times that of KDP. The dielectric behavior of TMA crystal was analysed by dielectric studies. The grown crystal exhibits negative phtotoconductivity.

Reference

1. V.G. Dmitrier, G.G.Gurzadyan, D.N. Nikogosyan, Hand book of nonlinear optical crystal, 2nd ed, Springer, New York, 1997.
2. M.S. Wong, C. Bosshard, F.Pan, P.Gunter, Adv. Mater. 8 (1996) 677.
3. S.Natarajan, S.A.Matrin Britto, E.Ramachandran, Crst. Growth Des. 6 (2006) 137.
4. C.Chen, N.Ye, J. Lin, J.Jiang, W. Zeng, B.Wu, Adv. Mater. 11 (1990) 1071.
5. H.W. Zhang, A.K. Batra, R.B. 137 (1994 Lai, J. Cryst. Growth) 141.
6. Dongfeng Xue, Siyuan Zhang, Physica B 262 (1999) 78.
7. M.D. Aggarwal, J. Choi, W.S. Wang, K. Bhat, R.B. Lal, A.D. Shields, B.G. Penn, D.O. Frazier, J. Cryst. Growth 204 (1999) 179.
8. S.S. Gupta, A. Marcarno, D. Pradhan, C.F. Desai, N.J. Melikechi, Appl. Phys. 89 (2001) 3949.
9. A. Arulchakkaravarthi, N. Balamurugan, P. Rakesh Kumar, S. Santhanaraghavan, T. Muralithar, Nagarajan, P. Ramasamy, Mater. Lett. 58 (2004) 1209.
10. P. Damodarana, P. Kumaresana, R. Rajasekaran, R. Jayavel, Journal of intense pulsed lasers and applications in advanced physics 1 (2011) 49.
11. A. Ruby, S. Alfred Cecil Raj, International Journal of ChemTech Research, 5 (2013) 482.
12. G.Madurambal, M.Mariappan, Indian journal of pure and applied physics, 48 (2010) 264.
13. Ramajothi., J., Dhanushkodi ,S., Nagarajan,K., Crystal Research and Technology 39 (2004), pp 414-420.
14. D.S. Chemla, J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, 1987.
15. A.A. Sukhorukov, YUSJ. Kivshar, Opt. Soc. Am. B 19 (2002) 772.
16. G.J. Maroulis, Chem. Phys. 113 (2000) 1813.
17. G.J. Maroulis, Mol. Struct. (THEOCHEM) 633 (2003) 177.
18. W.A. Schoonveld, J. Wildeman, D. Fichou, P.A. Bobbert, B.J. VanWees, T.M. Klapwijk, Nature 404 (2000) 977.
19. P. Srinivasan, T. Kanagasekaran, R. Gopalakrishnan, Cryst. Growth Des. 8 (2008) 2340.
20. P. Srinivasan, Y. Vidyalakshmi, R. Gopalakrishnan, Cryst. Growth Des. 8 (2008) 2329
21. K. Swaminathan and H.M.N.H Irving, J. Inorg Nucl.chem. 26, 1291 (1964)
22. Robert M. Silver stein and Francis x. Webster Spectrometric Identification of organic compounds, sixth edition , John wiley , and sous,Inc., Newyork (1998).
23. The Spectral Data Base System for Organic Compounds (SDBS) at The National Institute of materials and chemical research in Japan.
24. Ramajothi., J., Dhanushkodi ,S., Nagarajan,K., 2004, "Crystal growth , Thermal optical and Microhardness" studies of tris (Thiourea) Zinc sulphate- a Semiorganic NLO material "Crystal Research and Technology 39, pp 414-420.
25. Kumar K.Ramamurthy, K.A.novel growth method for zinc thiourea sulphate single crystals .cryst Res Technol.2006.41; 217-20 .
26. S.Krishnan, C.JustinRaj , S.M.Navis Priya, R.Robert ,S.Dinakaran,S.Jerome Das, Cryst.Res.Technol. 43(2008) 211.
27. S.Boomadevi, R.Dhanasekaran, J.Cryst.Growth, 261 (2004) 70.
28. S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39(1968)3798
29. J.S.Pan,X.W.Zhang,Acta.Master.54 (2006) 1343.
30. S.Pandi,D.Jayaraman,Mat.Chem.Physics 71(2001) 314.
31. R.H .Bube, Photoconductivity of solids ;New York, 1981.
32. V.N.Joshi; Photoconductivity, Marcel Dekker; New York,1990.