Synthesis, Growth, Spectral, Optical And Thermal Studies of An Organo Metallic Single Crystal - Bisthiourea Sodium Nitrate

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Abstract- *Organo metallic bisthiourea sodium nitrate (BTSN) was synthesized and single crystal was grown by solution growth method. Solubility of BTSN was determined in distilled water at different temperatures. Single crystal X-ray diffraction (XRD) study reveals that the crystal BTSN belongs to monoclinic crystal system. Powder X-ray diffraction peaks of the grown BTSN were indexed. The presence of functional groups and the co-ordination of metal ions to thiourea were confirmed by FTIR analysis. The UV- Vis spectrum shows the transmitting ability of the crystal in the visible region. Thermal stability of the TSN crystal was studied by thermal analyses (TGA/DTA/DSC). The mechanical hardness of the crystal was obtained using Vicker's micro hardness test. Kurtz powder second harmonic generation (SHG) measurement confirms the nonlinear optical (NLO) property of the grown crystal and the SHG value is comparable to KDP.*

I. INTRODUCTION

Nonlinear optical materials play a vital role in optical signal processing, optical communication, optoelectronics and optical computing. Intensive studies of linear and nonlinear optical parameters enable to fabricate materials, suitably designed at the molecular level for applications in optoelectronic devices. A continuous research has been carried out in growing organic, inorganic and semi-organic materials possessing wide transparency range, high laser damage threshold and high nonlinear optical coefficient which make them suitable for device fabrication [1]. Some organic complexes such as benzoyl glycine (BG) [2], L- alaninium maleate (LAM) [3], 4-N, N- dimethylamino- 4'- N- methyl-stilbazolium toyslate (DAST) [4] and 2, 6- dibenzylidenecyclohexanone (DBCH) [5] show moderate mechanical strength due to the molecules in pure organic crystals are often bonded by weak Van der waals forces or hydrogen bonds, which result in poor mechanical robustness and thermal properties. Particularly in semi-organic materials

the organic ligand is ionically bonded with inorganic host and the material relatively gets higher mechanical strength and greater chemical stability [6]. Semi organic materials possess several attractive properties such as high NLO coefficient, high laser damage threshold and wide transparency range, high mechanical strength and good thermal stability, which make the materials suitable for second harmonic generation (SHG) and other NLO applications. A series of studies on semi organic amino acid compounds such as L- arginine hydrobromide (L- AHBr) [7], L- histidine tetrafluoroborate (L- HFB) [8], glycine sodium nitrate (GSN) [9] and L- alanine sodium nitrate (LASN) [10] as potential NLO crystals have been reported. Among these crystals, the second harmonic generation efficiency (SHG) of glycine sodium nitrate and L- alanine sodium nitrate crystals was two times that of potassium dihydrogen orthophosphate (KDP)

Thiourea is a simple organic material with high crystallographic symmetry which crystallizes in the rhombic bipyramidal division of the rhombic system [11]. The thiourea crystal structure has established the coplanarity of the C, N and S atoms in the molecule [12]. Also thiourea molecule is an excellent inorganic matrix modifier due to its large dipole moment and has the ability to form an extensive network of hydrogen bonds [13, 14]. The thiourea molecule can also combine with metal ions to form stable metal complexes which exhibit wonderful linear and nonlinear optical activity [15]. Such metal complexes of thiourea have possessed improved properties when compared with the individual properties of the organic and the inorganic molecules [16]. Some of the metal complexes of thiourea reported are bisthiourea zinc chloride [15], bisthiourea cadmium chloride, tetra thiourea copper (I) chloride and zinc thiourea sulphate [17- 19]. We report in this work on the synthesis, growth and characterization of the semi organic single crystal of bisthiourea sodium nitrate for the first time.

II. EXPERIMENTAL PROCEDURE

2.1 Synthesis

Bisthiourea sodium nitrate (BTSN) was synthesized from commercially available AR grade thiourea (CS $(NH_2)_2$) and sodium nitrate ($NaNO_3$) by mixing them in distilled water in the 2:1 ratio according to the reaction.

$$2[CS\ (NH_2)_2] + NaNO_3 \rightarrow Na\ [CS\ (NH_2)_2]_2\ NO3$$
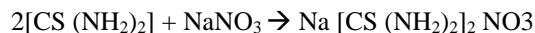
The calculated amount of thiourea was first dissolved in distilled water. Then sodium nitrate was added slowly to the solution with continuous stirring for six hours at temperature 40˚C. The prepared solution was let to dry at the same temperature. The product was purified by repeated recrystallization process and was used for crystal growth.

2.2 Growth of BTSN crystal

The solubility of BTSN was determined at four different temperatures (30°C, 35°C, 40°C and 45°C) by dissolving the solute in distilled water. The container containing the BTSN solution was placed in a constant temperature bath (CTB) maintained at the desired temperature and the solution was stirred and saturated. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The synthesized salt was dissolved in distilled water and thoroughly mixed using a magnetic stirrer to ensure homogeneous concentration throughout the volume of the solution. The pH value of the solution was 4.9 at 30°C temperature. The saturated solution prepared at 30°C was taken in a beaker, covered with perforated paper and placed in the CTB at 30°C and left undisturbed for slow evaporation. Good quality single crystals of BTSN were grown in 30 days and is shown in Fig.1.
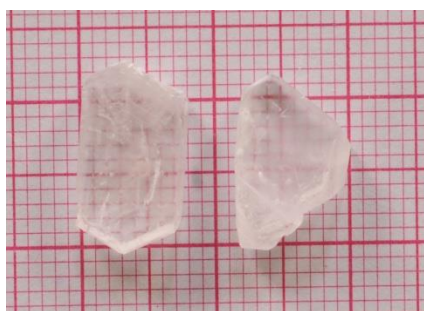

Fig.1: As grown crystals of BTSN

III. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

The lattice parameters of BTSN were determined by single crystal XRD studies using an ENRAF NONIUS CAD-4 diffractometer with Mo K_α (λ=0.71073Å) radiation to estimate the lattice parameter. Single crystal XRD study reveals that

BTSN belongs to monoclinic crystal system (β= 90.13°). In order to reveal the role of metal ions with thiourea complexes, a comparison is made between the cell parameters of thiourea (TU), bisthiourea cadmium chloride (BTCC), sodium nitrate (SN), bisthiourea zinc chloride (BTZC), zinc thiourea sulphate (ZTS), bisthiourea sodium fluride (BTSF) with BTSN in Table 1

Table 1:Comparison of Lattice parameters of TU, SN, BTCC, BTZC, ZTS, BTSF and BTSN.

Samples	a(Å)	b(Å)	c(Å)	Volume (A)³	Crystal Structure	Ref.
TU	7.66	8.54	5.52	360.7	Orthorhombic	[20]
SN	5.06	-	16.80	373.5	Rhombohedral	[JCPDS]
BTCC	5.81	6.48	13.10	494.1	Orthorhombic	[17]
BTZC	5.90	12.75	12.97	979.5	Orthorhombic	[15]
ZTS	11.11	7.79	15.47	1340.1	Orthorhombic	[19]
BTSF	6.49	7.79	9.60	493.6	Orthorhombic	[21]
BTSN	7.64	5.47	8.54	357	Monoclinic	Present work

Powder XRD analysis was carried out using a Rich Seifert diffractometer with Cu K_α (λ=1.54059Å) radiation. X-ray diffraction pattern was recorded by crushing the grown crystal into fine powder and sample was scanned over the 2θ range 10-80° at a rate of 1° per minute. The well defined peaks at specific 2θ values showed a high degree of crystallinity of the compound. Powder XRD peaks of this work were indexed using Check cell software and are shown in Fig.2.
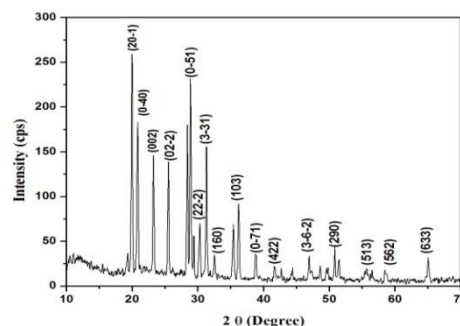

Fig.2 Powder x-ray diffraction spectrum of BTSN

3.2 FTIR Spectral analysis

Thiourea molecule has a sulphur atom and two nitrogen atoms capable of being co-ordinated to a metal atom [22]. In thiourea metal complex crystals there are two possibilities by which the co-ordination can occur with metal ions. The metal co-ordination and the vibrational analysis on M [(TU) $_2$] X$_2$, (M= Zn, Cu, Hg, Pb, Ti and Pt, TU = thiourea and X-halogen) type of molecules was reported by Swaminathan and Irving [23]. The sample was prepared by KBr pellet method. The Fourier transform infrared spectrum of BTSN was recorded in the frequency region of 400- 4000 cm^{-1} using Perkin Elmer spectrum and is given in Fig. 3. Metal coordination of thiourea in BTSN is expected to influence the vibrational frequencies of thiourea especially those of NH$_2$ stretching and C=S stretching vibration.
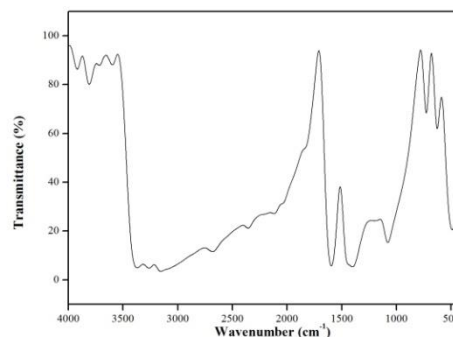
In the high wave number region of the spectrum, the absorption peaks are often dominated by symmetric and asymmetric stretching modes of NH$_2$ present in the grown crystal BTSN. In metal organic complexation the bands in this region are shifted to high wave number side. This may be due to sulphur to metal bond in the grown crystal resulting in the increase of the double bond nature of the carbon to sulphur bond [24, 25]. The asymmetric stretching vibration of NH$_2$ group of BTSN is found around 3371 cm^{-1}. The N-C-N stretching vibration frequency is observed at 1594 cm^{-1} in the spectrum of BTSN corresponds to 1477 cm^{-1} absorption of free ligand thiourea. The increase in the frequency can be attributed to the greater double bond character of the carbon to nitrogen bond on complex formation. If the bonding is made through sulphur, there will be a decrease in the C-S stretching frequency and an increase in the C-N stretching frequency. This phenomenon would be reverse, if the bonding is through nitrogen [26]. In the Fig.4 the band corresponding to C=S stretching vibrations is appeared at 1403 cm^{-1}. A comparison of vibrational frequencies of various functional groups is made among various thiourea complexes such as (Cu (TU) $_6$ Br$_2$) [27], bisthiourea zinc acetate (BTZA) [28], tetrakis thiourea potassium iodide (TTPI) [29] with BTSN. The IR band at 1078 cm^{-1} in BTSN corresponds to NH$_2$ rocking vibration which is identified at 1089, 1134, 1090 and 1082 cm^{-1} in Cu (TU) $_6$ Br$_2$, BTZA, TTPI and free ligand thiourea respectively. In these metal complexes of thiourea, NH$_2$ rocking vibration wave number is shifted to higher wave number when compared to that of free ligand (TU). The increase in frequency is due to the greater double bond character of the carbon to nitrogen bond on complex formation. Similarly, C-N symmetric stretching vibration in the BTSN crystal is at 726 cm^{-1}

. Fig. 3   : FTIR spectrum of BTSN

3.3 Optical spectral analysis

Linear optical properties of the crystals were studied using a Perkin Elmer-Lambada 35 UV-Vis spectro photometer. The optical absorption spectrum gives us valuable information about the structure of the molecule because the absorption of UV and visible light involves excitation of electrons in σ and π orbitals from the ground state to a higher energy state. The recorded optical absorption spectrum in the wavelength range between 190 and 1100 nm is shown in Fig. 4. The UV lower cut off wavelength occurs at 235 nm. As the crystal is transparent in the entire visible and near infrared region it can be used as a potential material for frequency doubling.
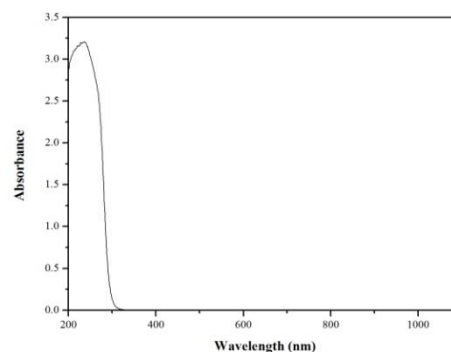

Fig. 4   : Absorption spectrum of BTSN

3.4 Thermal analysis

Thermograms such as TGA, DTA and DSC were recorded for the grown crystal using SDT Q600V 8.3 instrument. Micro hardness studies were carried out using Shimadzu make model HMV- 2 instrument. The thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) give information regarding, the presence of water molecule in the grown crystal, phase transition and different

stages of decomposition of the crystal system [30]. A powdered sample of BTSN weighing 2.3150 mg was used for the analyses. The analyses were carried out simultaneously in nitrogen atmosphere at a heating rate of 20°C/min for a temperature range 20- 1200°C and are shown in Fig. 5. TGA shows a weight loss at 53.69°C which may be due to the presence of physically adsorbed water molecule in the sample [31]. The TGA curve also shows that there was a major weight loss of about 65.81% in the temperature range 182- 242°C. The nature of the weight loss indicates the decomposition point of the material. The DTA curve shows that the first exothermic peak at 164.82°C and then the sample undergoes two irreversible endothermic transitions. The first endothermic peak at 186.40°C may be due to the liberation of volatile substances and the second intense endothermic peak at 235.4°C indicates the major decomposition point of the material. The decomposition temperature of thiourea is 182°C [32]. The decomposition temperature of BTSN at 235.4°C shows the formation of metal complex of thiourea. The decomposition temperature of BTSN is higher than that of other semi organic crystals of thiourea like BTNC [33] (221.08°C), TTPI [29] (183.3°C) and CTA [34] (206°C). The increase in decomposition temperature of semi organic materials when compared with other organic crystals arises due to the stronger bonding existing between the conjugation layers of thiourea molecules and metal ion [35]. High temperature differential scanning calorimetry spectrum of the BTSN was recorded. The scan was run from 20°C temperature to 1200°C, two peaks were observed. The specific heat of BTSN crystal at 234.64ºC was found to be 1314J/g/°C.
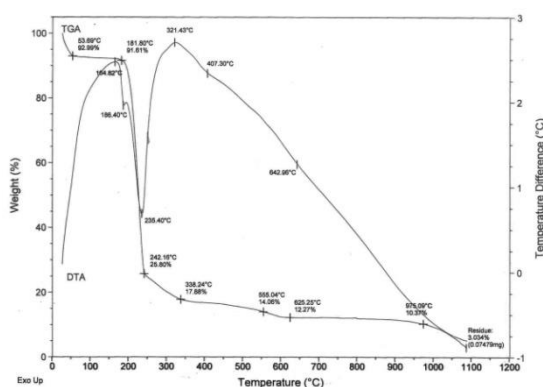

Fig. 5   : TGA / DTA curves of BTSN

3.5 Microhardness Test

Microhardness measurement is a general microprobe technique for assessing the bond strength of the sample apart from being a measure of bulk strength. Hardness of a material is a measure of the resistance that it offers to the local deformation caused by indentation. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation. The crystal of 3mm thickness was used to avoid the surface defects which influence the hardness value strongly [36]. Microhardness studies were carried out at room temperature using Shimadzu make model HMV 2 fitted with Vicker's pyramidal indenter. The load (P) was varied from 25 to 100 g and the time of indentation was kept constant at 5s for all trials. The average value of diagonal lengths of indentation was measured. The hardness of the material H_v was calculated by the relation.

$$H_v = 1.8544P/d^2 \ (Kg/mm^2)$$

Where P is the applied load in Kg and d is the diagonal length of the indentation impression in mm. A graph was plotted for hardness H_v versus P and is shown in Fig. 6. Work hardening coefficient (n) was estimated from a graph drawn between log P and log d which is a straight line. The slope of this graph gives value of n equals to 2.7. From the prediction of Onitsch [37] the value of n lies below 1.6 for hard materials and it is more than 1.6 for soft materials. As the value of n for BTSN is 2.7, BTSN belongs to soft material class and hence the hardness of BTSN increases with the increase in load which confirms the reverse indentation size effect [38, 39].
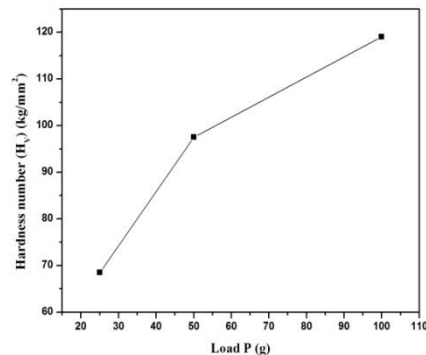

Fig. 6   : Vickers's hardness H_v versus load P for BTSN crystal

3.6. Nonlinear optical studies

The second harmonic generation (SHG) efficiency of BTSN was determined by the modified version of the powder technique developed by Kurtz and Perry [40], using a Nd: YAG, 10 ns laser with a pulse rate of 10 Hz working at 1064 nm. The incident laser power was chosen as 9.6mJ pulse energy. The SHG was confirmed by the emission of green radiation (λ= 532Å) which was finally detected by a photomultiplier tube (PMT) and displayed on the oscilloscope (CRO). The optical signal incident on the PMT was converted into voltage output at the CRO and its value for BTSN is 30

mV and that for standard KDP is 32 mV. So, the powder SHG efficiency of BTSN is 94% of KDP.

IV. CONCLUSION

Bisthiourea sodium nitrate was synthesized by the reaction of thiourea with sodium nitrate in water. A single crystal of BTSN was grown from the aqueous solution by slow evaporation method. The unit cell parameters obtained from single crystal X-ray diffraction study show that BTSN belongs to monoclinic crystal system. The sharp peaks of powder XRD spectrum show high degree of crystallinity. FTIR spectrum of the grown crystal confirms the presence of various functional groups and the vibrational frequencies compared with compounds containing thiourea molecules are in good agreement. The optical absorption spectrum reveals that the crystal is transparent in the visible and NIR region. TGA/DTA studies showed the thermal stability of the grown crystal. The specific heat of BTSN crystal at 234.64°C is 1314J/g/°C. The Vicker's microhardness test shows that the hardness value increases with load, which confirms the reverse indentation size effects and the soft nature of the crystal. The powder SHG efficiency of BTSN was found to be 0.94 times that of KDP and hence suitable for frequency conversion application.

V. ACKNOWLEDGEMENT

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