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Growth and characterization of semi-organic nickel bis thiourea nitrate single crystal

V. Revathi* and V. Rajendran

Department of Physics, Presidency College, Chennai, India

ABSTRACT

Nickel Bis Thiourea Nitrate (NBTN) a semi organic nonlinear optical material has grown by slow evaporation of mixed ethanol and de-ionized water solution at room temperature. The grown crystals were subjected to characterize by Single crystal X-ray diffraction, Fourier transform infrared spectroscopy, optical transmission spectral analysis, dielectric studies, thermal analysis, and indentation tests. Single crystal X-ray diffraction studies confirm that the crystal belongs to monoclinic structure. The nature of co-ordination and the functional groups present were investigated by the Fourier transform infrared spectrum. Its optical behavior was examined by UV-Vis-NIR spectrum and found that the crystal is transparent in the region between 500-1100 nm. Dielectric constant and dielectric loss for various frequencies and temperature were carried out to the as grown crystals. The thermal analyses confirmed that the crystal is stable upto 184◦C. The mechanical strength of the crystal was studied using Vickers microhardness tester.

Key words: Slow evaporation method, Semi organic crystal, Thiourea, Microhardness, Dielectric studies

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INTRODUCTION

Metal-organic compounds as NLO materials have attracted much more attention for their high NLO coefficients, stable physco-chemical properties and better mechanical intension. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment [1] and its ability to form an extensive network of hydrogen bonds [2]. The metal complexes of thiourea which have low UV cut off wavelengths, applicable for high power frequency conversion have received much attention. Ligands like thiourea form stable complexes through coordinated bonds by S and N donors which are adequate to combine with metal [3]. The centrosym- metric thiourea molecule, when combined with inorganic salt yields noncentrosymmetric complexes, which have the NLO properties [4] and also some of them found centrosymmetric in nature[5-7].The metal-organic complexes of thiourea such as zinc tris thiourea chloride (ZTTC) have already been reported by us [8]. The structural determination of Hexakis(thiourea)nickel(II) nitrate crystals (HTNN) were carried out by J. Madar et al (9) and M.P. Rodriguez et al (10) and their redetermination had done by M.M.U. Mehboob et al (11). The various studies of HTNN crystal were carried out by K. Muthu et al (12). In this present study, the growth of single crystals of Nickel Bis thiourea nitrate (NBTN) by slow evaporation method and its characterization have been studied.

MATERIALS AND METHODS

Experimental details

Analytical grade thiourea and nickel nitrate (AR grade) was taken in equimolar ratio (1:1) and dissolved in mixed ethanol and de-ionized water solvent. In order to reduce the growth period, mixed solvent was chosen. The solution was stirred by magnetic stirrer. Once got the clear homogenous solution it was filtered by whatman filter paper to remove the insoluble impurities and allowed to dry at room temperature. The required quantity of nickel nitrate and thiourea were estimated from the following reaction:

$$2[CS(NH_2)_2] + Ni(NO_3)_2 \rightarrow [Ni[CS(NH_2)_2]_2](NO_3)_2$$

The NBTN crystals of dimension 13×13×3 mm^3 were grown within a period of 10 days. The crystal was further purified by repeated re-crystallization process. The photograph of the as grown crystal is shown in Fig. **1** and growth conditions are given in table **1**.

Fig.1.As grown crystal of NBTN single crystal

Table.1. Growth conditions

Solute	Thiourea and Nickel nitrate
Molar ratio	2:1
Solvent	De-ionized Water and ethanol (1:1)
Method	Slow evaporation
Growth Period	10 days
Purification	Re-crystallization
Size of the crystal	13*13*3 mm^3

Characterization techniques

Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction analysis of grown crystal was carried by BRKER axs SMART APEXII diffractometer to determine lattice cell parameter. The collected data of lattice cell parameters are a = 22.33 Å, b = 9.19 Å, c = 17.29 Å and cell volume = 2652 $Å^3$. The crystal belongs to monoclinic system with space group C2/c. The crystal data is reported in Table **2** and it agrees well with the earlier reported values [9-12].

Table.2. Crystal data for crystal

Chemical formula	$[Ni[CS(NH_2)_2]_2](NO_3)_2$
Crystal System	Monoclinic
Space group	C2/c
a(Å)	22.33
b(Å)	9.19
c(Å)	17.29
α(deg)	90
β(deg)	133.79
γ(deg)	90
Volume(A^3)	2652
Crystal color	Green

Spectral analysis

The Fourier transform Infrared transmission spectrum (Fig**. 2**) of NBTN crystal was recorded in the region 400–4000 cm^{-1} from KBr pellets on a Perkin Elmer FT-IR spectrometer. The band 2750-3700 cm^{-1} represents the Symmetric and asymmetric stretching of NH_2 molecule. The region 2390.85 represents N-H stretching. The peak at 1490.30 in the spectra is assigned to -CN stretching. Absorption band at 1360.26 cm^{-1} is in the spectra due to -NO stretching. The absorption at 1093.84 cm^{-1} can be assigned to -CN stretching. The peak at 712.74 cm^{-1} in the spectra is attributed to C=S stretching. The region at 3492 cm^{-1} represents the S-S stretching. The observed absorption peaks/bands of NBTN sample are given in Fig.**2** and all the functional group assignments are summarized in Table.**2**.

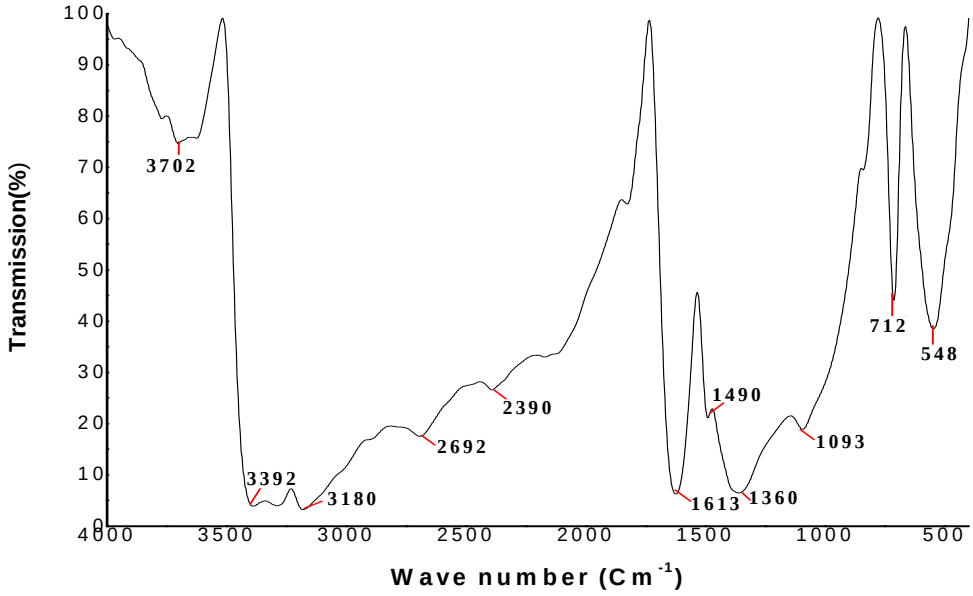

Fig .2.FTIR spectrum of NBTN single crystal

Table. 3. Assignments of IR band frequencies (cm^{-1}) of NBTN crystal

Wave number (Cm^{-1})	Band assignments
548.38	S-S stretching
712.74	C=S stretching
1093.84	-CN stretching
1360.26	-NO stretching
1490.30	-CN stretching
1623.42	N-H bending
2390.85	N-H stretching
2750-3700	Symmetric and asymmetric stretching of NH_2

UV-visible spectral study

The transmission spectrum obtained between 190 and 1100 nm using Lambda 35 that the transmittance was in the range 500–1100 nm with the cutoff wavelength 358 nm, which is required for the materials exhibiting NLO properties.

Thermal analysis

Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) of NBTN were carried out in nitrogen atmosphere from 25–978 °C, using SDT Q600 V8.0 Build 95. The TGA and DTA traces of NBTN are shown in Fig **3**. DGT decomposition starts at 184 °C, there is some weight loss in the range between 50 °C and 180 °C is recorded. This illustrates the presence of physically adsorbed or lattice water in the crystal. Hence the compound is stable up to 184.57 °C. From the TGA curve of the DGT shows four-stage decomposition at 177, 208, 282 and 516 °C. The maximum weight loss (47.03%) observed between 208 to 232 °C may be due to the discharge of volatile substances like ammonia, nitric oxide etc. The total weight losses and the resulting residue (0.3%) are stable up to 978°C. This crystal can be used for any applications up to the temperature 184°C.

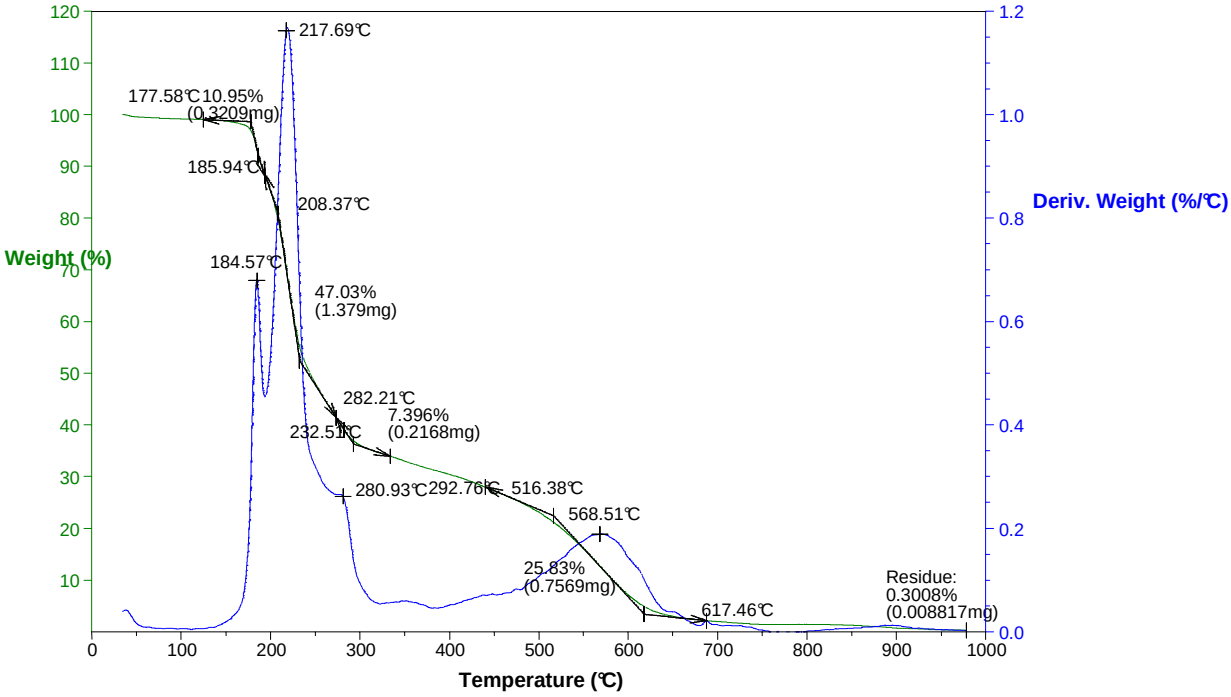

Fig.3. TG-DTA analysis of NBTN

Dielectric studies

The dielectric characteristics of the material give the information about the nature of atoms, ions, bonding and their polarization mechanism in the material. An NBTN single crystal was subjected to dielectric study using a HIOKI HITESTER model 3532–50 LCR meter. The sample of dimension 9.54×6.66×3.41 mm^3 was taken to this study. The surface of the sample was coated with silver paste for firm electrical contact. The experiment was carried out in the frequency range 500 Hz– 5 MHz at different temperatures (313,323 and 333 K) to find the capacitance of the sample. The dielectric constant and dielectric loss of the crystal are measured to the frequency and temperature mentioned and shown in Fig.**4** and **5.** It is noted from the Fig.**4** that the dielectric constant decreases exponentially with increasing frequency at different temperature. The value of dielectric constant is high at low frequency because of the presence of all the four polarization but not at high frequency by the presence of only space-charge polarization. Only at 50 Hz dielectric constant increases to the increase in temperature and all increasing frequency have the same value of dielectric constant with respect to temperature.

It is evident from the Fig. **5** that the value of dielectric loss is also decreases with increasing frequency.

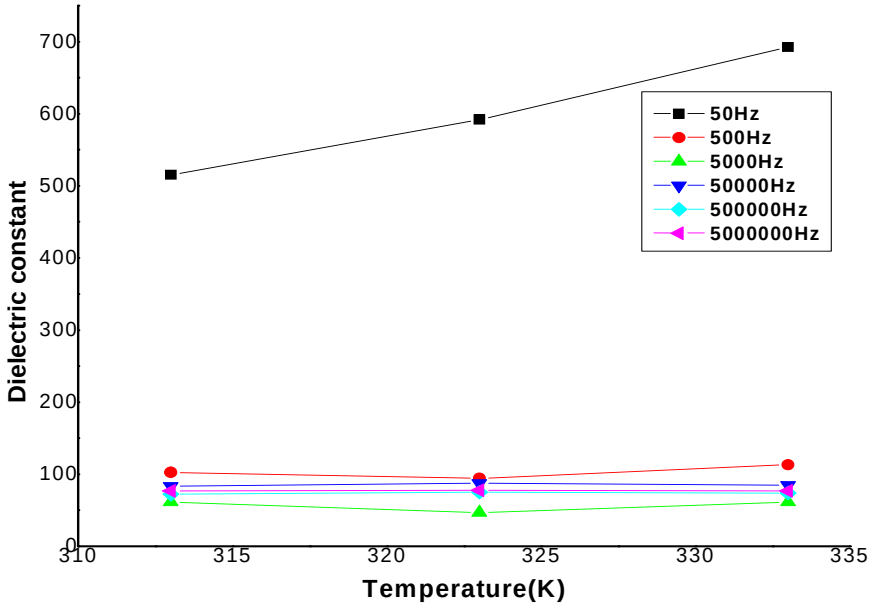

Fig.4.Dielectric constant of NBTN crystal with log frequency

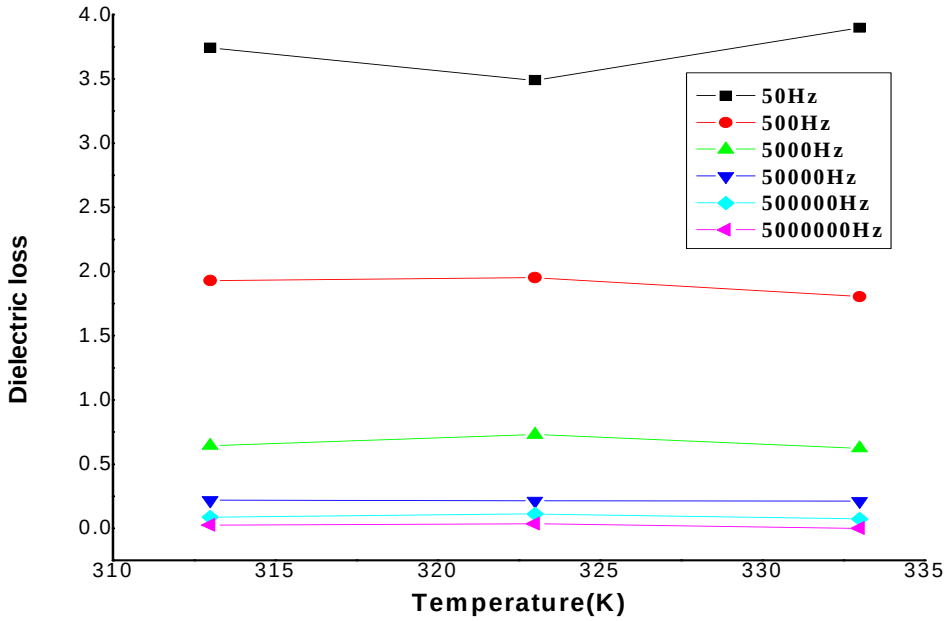

Fig.5. Dielectric loss of NBTN with log frequency

Indentation tests

Microhardness testing is to be performed on crystals to evaluate the mechanical properties by measuring the resistance of the lattice against the applied load [13]. It furnishes the local deformation caused by indentation. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation. A transparent polished crystal free from cracks was placed on the platform of Vickers microhardness tester .The indentations were

made on the flat surface with the load ranging from 25 to 100 g using Shimadzu HMV-2T fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The indentation time has been kept 5 seconds for all the loads. Several indentations were made for each load and the diagonal length (d) of the indented impressions was measured. The Vickers hardness number of the materials Hv is determined by the relation, $Hv=1.8544\ P/d^2$ kg/mm^2.

Where P is the applied load in kg and d is the diagonal length of indentation impression in mm. The hardness number was found to increase with load and above 100 gm; cracks were developed on the smooth surface of the crystal due to the release of internal stress generated locally by indentation. The average value of the Vickers hardness number for the grown crystal is 100 kg/mm^2. The plot drawn between the corresponding loads and hardness values of NBTN is shown in Fig.**6**.

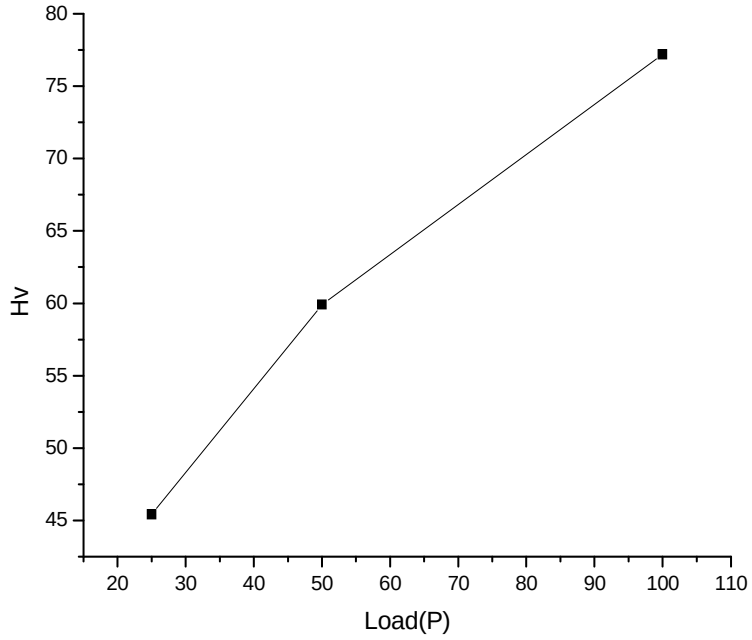

Fig.6. Microhardness Curve of NBTN crystal

CONCLUSION

Single crystals of NBTN were grown using mixed ethanol and water solution by slow solvent evaporation method. The crystal is confirmed with X-ray diffraction analysis; the crystal belongs to the monoclinic system. The FTIR analysis confirms the bonding interaction and functional group present in the grown crystal. Dielectric studies show that the dielectric constant and dielectric loss decreases with increase in frequency. From the TGA and DTA curves, the sample is highly stable upto 184˚C which indicates that the material is thermally stable. Mechanical strength of the crystal has been studied by Vickers microhardness measurements.

REFERENCES

[1] K.H. Hellwege, A.M. Hellwege, Landolt–Bornstein: Numerical Data and Functional Relationships in Science and Technology Group II, Springer, Berlin, **1982**.
[2] S.G. Bhat, S.M. Dharmaprakah, *Mater. Res. Bull.*, **1998**, 33,833.
[3] N. Karthick, R.Sankar , R.Jayavel , S.Pandi, *J. Cryst. Growth*. **2009**, 312,114.
[4] S. Anie Roshan, Cyriac Joseph, M.A. Ittyachen, *Mater. Lett*. **2001**, 49.
[5] G. SenthilMurugan, P. Ramasamy, *J. Cryst. Growth*.**2009**, 311,585.
[6] M. Lydia Caroline, S. Vasudevan, *Mater.Chem.Phys*.**2009**, 113,670.

[7] G. Senthil Murugan, N. Balamurugan, P. Ramasamy, *Mater. Lett.***2008**, 62, 3087.
[8] V. Revathi, V. Rajendran, *Recent Research in Science and Technology* **2012**, 4, 2, 38.
[9] J. Madar, *Acta Crystallographica*.**1961**, 14,894.
[10] M.P. Rodriguez, M. Cubero, R. Vega, A. Morente, J.L. Vazquez, *Acta Crystal- lographica* **1961**,14,1101.
[11] M.M.U. Mehboob, M. Akkurt, I.U. Khan, S. Sharif, I. Asif, S. Ahmad, *Acta Crystallographica E*.**2010**, 66, i57.
[12] K. Muthu, S.P. Meenakashisundaram, *J. Cryst. Growth*.**2012**, 352,158.
[13] J.B. Quinn, G.D. Quinn, *J. Mater. Sci*.**1997**, 32, 4331.