

Growth and Characterization of Bisthiourea Nickel Bromide—New Semiorganic Nonlinear Optical Crystal

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ABSTRACT

A new semiorganic nonlinear optical crystal of bisthiourea nickel bromide (BTNB) was grown successfully by slow evaporation technique using water as solvent. The lattice parameters of the grown crystal have been determined by X-ray diffraction studies. Vibrational spectrum is recorded to determine symmetries of molecular vibrations. Optical absorbance spectrum recorded revealed that this crystal has good transparency in the visible region. The second harmonic generation test of BTNB confirmed the nonlinear nature of the crystal. The BTNB crystal was analyzed by a differential thermal analysis and thermogravimetric analysis (DTA-TGA) to obtain its thermal stability. Vickers microhardness test done on the crystal shows that the crystal has greater physical strength.

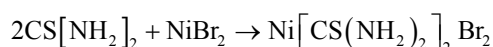
Keywords: BTNB—Bisthiourea Nickel Bromide; SHG—Second Harmonic Generation; TGA/DTA; NLO—Nonlinear Optical

1. Introduction

Nonlinear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical storage technology. The search for new frequency conversion materials over the past decade has led to the discovery of many semiorganic NLO materials with high nonlinear susceptibilities. Among the semiorganic NLO materials metal complexes of the thiourea having lower cut off wavelengths, applicable for frequency conversion are of interest because both organic and inorganic components in it contribute specifically to the process of SHG [1-7]. In the present work metal replacement is studied by taking a reported NLO crystal bisthiourea cadmium bromide [8]. Here the metal cadmium is replaced by nickel which is more active electro chemically.

2. Experimental

High purity salts (99.9%) purchased from E-Merck were used for the crystal growth experiments. Single crystals of bisthiourea nickel bromide (BTNB) were grown at room temperature by slow evaporation of on aqueous solution containing thiourea and nickel bromide in stoichiometric ratio 2:1 as per the reaction.



Colourless crystals were harvested in about 110 days and are shown in **Figure 1**.

3. Characterization

Single crystal XRD analysis was carried out using on Enraf Nonius CAD-4. X-ray diffractometer with $M_0 K_\alpha$ ($\lambda = 0.770 \text{ \AA}$) radiation to identify the structure and to

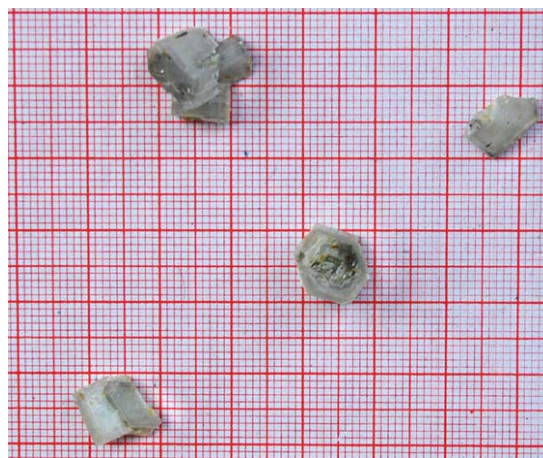


Figure 1. Photograph of the grown BTNB crystals.

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presence of functional groups in BTNB qualitatively, estimate lattice parameter values. In order to analyze the Fourier transform of infrared (FT-IR) spectrum was recorded in the range $400 - 4000 \text{ cm}^{-1}$ using Perkin Elmer grating infrared spectrometer. The sample was in a pellet form in KBr phase. Linear optical properties of the crystals were studied using Varion Carey 5E UV-Vis-NIR spectrophotometer. Thermal studies were carried out using simultaneous thermogravimetric analyser (STA) 409C [NETZSCH]. The nonlinear property of BTNB crystals was confirmed from second harmonic generation test by using Nd:YAG laser beam. The physical strength of the crystal was measured by Vicker's micro hardness test.

4. Results and Discussion

4.1. X-Ray Diffraction Studies

The single crystals of BTNB have been subjected to X-ray diffraction studies using an ENRAF NONIUS CAD4 X-ray diffractometer to determine the cell structure and cell parameters. The studies revealed that the crystal belongs to orthorhombic system. In order to understand the role of metal ions in the grown crystals, a comparison is made between free ligand thiourea, bisthiourea cadmium bromide and bisthiourea nickel bromide and is given in **Table 1**.

4.2. Analysis of IR Spectrum of Thiourea Vibrations in BTNB

The IR spectrum of the free ligand and its transition metal complex bisthiourea cadmium bromide (BTCB) was reported earlier [8]. In the present study an attempt has been made to reveal the effect of coordination on the vibrational bands of the ligand, when Nickel replaces Cadmium. In the FT-IR spectrum (**Figure 2**) of BTNB, the NH stretching vibrational bands of NH_2 were observed at 3376 and 3268 cm^{-1} . The NH_2 bending vibration which was observed at 1614 cm^{-1} for BTCB is found at 1601 cm^{-1} for BTNB. In BTCB the C-S stretching vibration was found at 1434 cm^{-1} whereas it was recorded at 1410 cm^{-1} for BTNB. The IR band for NH_2 rocking was observed at 1096 cm^{-1} for BTCB is recorded at 1080 cm^{-1} for BTNB. The symmetric stretching band is recorded at 716 cm^{-1} and 726 cm^{-1} for BTCB and BTNB respectively. The IR band of N-C-S bending vibration is observed at 555 cm^{-1} for BTCB whereas it is observed at 494 cm^{-1} for BTNB. This study (**Table 2**) reveals that when nickel replaces cadmium, the corresponding vibrational frequencies are greatly altered.

4.3. Optical Transmission Spectrum

Optical absorption spectrum (**Figure 3**) of BTNB was

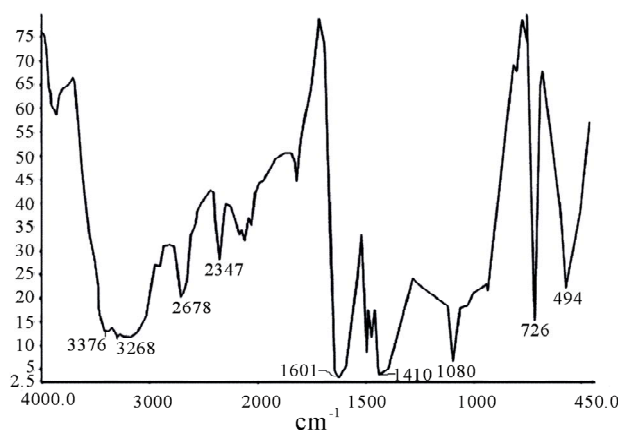


Figure 2. FT-IR Spectrum of the grown BTNB crystals.

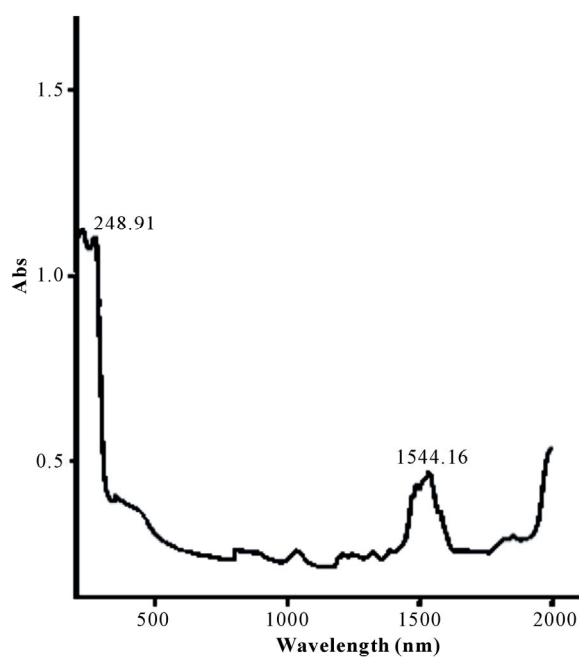


Figure 3. Absorbance spectrum of the grown BTNB crystals.

recorded by employing Varion Carey 5E UV-Vis-NIR spectrophotometer in the range $200 - 2000 \text{ nm}$. The lower cut off for BTNB is observed at 248.91 nm whereas it was observed at 269 nm for BTCB. The shifting of lower cut off in UV region further recommends the crystal for optoelectronic applications. The crystal has sufficient transmission in the entire visible region.

4.4. Second Harmonic Generation

The SHG of BTNB single crystal was studied using Nd:YAG laser (model continuum YG501C, $\lambda = 1064 \text{ nm}$) by Kurtz-Perry technique [9]. Powdered sample of the investigated crystal was taken in a glass capillary tube. It was irradiated by the laser pulse and second harmonic signal was detected using an optical cable attached to

Table 1.

S.No	Sample	a (Å)	b (Å)	c (Å)	A (°)	B (°)	Γ (°)	Volume (Å ³)
1	Thiourea	7.655	8.537	5.520	90	90	90	360.732
2	BTCB	5.6949	6.6051	7.5937	90	90	90	285.639
3	BTNB	6.1310	8.0907	9.1131	90	90	90	352.838

Table 2.

IR TU cm ⁻¹	BTCB cm ⁻¹	BTNB cm ⁻¹	Assignment
3380	-	3376	ν(N-H)
3279	3297	3268	ν(N-H)
1620	1614	1601	δ(N-H)
1477	1468	-	ν(N-C-N)
1414	1434	1410	ν(C-S)
1082	1096	1080	ρNH ₂
730	716	726	ν(C-N)
494	555	494	δ(N-C-S)

ν—Stretching; ρ—rocking; δ—deformation.

fluorescence spectroscopy (Princeton instrument Int. Spectroscopy instrument GmbH, model DIDA-512 GIR). The SHG output of the BTNB crystal was found to be 68 mV which is lesser when compared with SHG output of BTCB (98 mV) for laser beam of same intensity. The SHG output confirms the nonlinear nature of the experimental crystal.

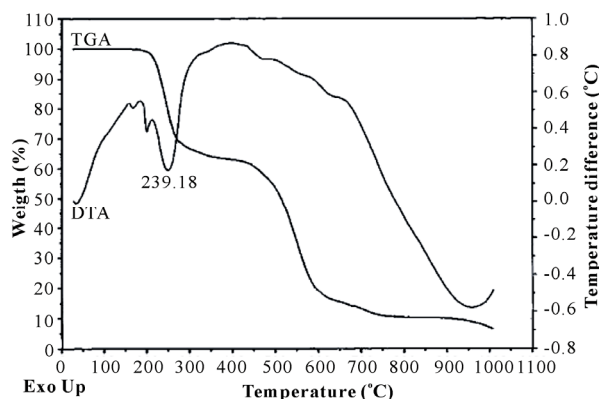
4.5. TGA/DTA-Analysis

The thermo gravimetric analysis and differential thermal analysis (TGA and DTA) curves for BTNB were obtained by using simultaneous thermo gravimetric analyser (STA) 409 C (NETZSCH) at a heating rate of 10°C/min in nitrogen atmosphere and are reported in **Figure 4**. The TGA curve shows that there was a weight loss of about 76% in the temperature range 182°C - 607°C.

The first endothermic peak at 189.08°C in the DTA curve may be due to the liberation of bromide and the second endothermic peak at 239.18°C may be due to liberation of thiourea in BTNB. The loosely bound nature of bromide in the grown crystal is confirmed by the formation of pale yellow precipitate which is sparingly soluble in ammonia when the powdered sample of the grown crystal is treated with silver nitrate in acid medium.

4.6. Microhardness Studies

Vicker's microhardness test conducted on the experimental crystal proves its greater physical strength. It is well explained by the increase in hardness value with increase in Load (**Table 3**).

**Figure 4.** TGA/DTA curves of the grown BTNB crystals.**Table 3.**

Load grams	BTNB HV
25	39.3
50	52.4
100	71.7

5. Conclusion

Single crystals of BTNB a new semi organic NLO material have been grown from aqueous solution. A detailed comparison of vibrational data of BTNB with BTCB reveals that when nickel replaces cadmium, they are greatly altered. The optical absorption spectrum shows that lower cut off for BTNB is smaller than that of BTCB. The SHG output confirms the nonlinear nature of the crystal. The TGA/DTA curves and Vicker's microhardness test confirms the thermal stability and physical strength of the investigated crystal.

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