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Influence of thiourea on the nonlinear optical properties of ammonium penta borate

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ABSTRACT

The bulk single crystals of thiourea doped ammonium penta borate were grown by slow evaporation solution growth technique using deionized water as solvent. The grown crystals were characterized by single crystal and powder X-ray diffraction, FTIR spectral analysis. The range and percentage of optical transmission were ascertained by UV-Vis-NMR spectrum. Its second harmonic generation relative efficiency was measured by Kurtz and Perry powder technique using Nd:YAG laser. Thermal properties were investigated by TG-DTA and DSC analyses.

Keywords: Crystal growth; Slow evaporation technique; Semi organic; SHG efficiency.

INTRODUCTION

The fast development in the field of opto electronics has stimulated the search for highly new nonlinear optical crystals for efficient signal processing. New nonlinear optical (NLO) frequency conversion materials can have significant impact on laser technology [1], Optical communication [2], and optical data storage technology [3]. Materials with nonlinear electro optical properties have a role in modern opto electronics that is analogous to that of nonlinear electronic circuit elements in conventional electronics. Inorganic borates exits in numerous structural types and some crystals such as KB_5 and BBO are excellent nonlinear optical materials, particularly in the UV region. These borate crystals generally posses chemical stability, high damage threshold and high optical quality, as well as wide range of transparency far into the ultraviolet on account of the rather large difference in the electronegative of B and O atoms [4]. The properties determining an effective NLO material particularly, the borate compound materials have been discussed and reviewed by several researchers [5-9]. In this series ammonium penta borate $(NH_4)_2O_5B_2O_3.8H_2O$ is one such efficient nonlinear optical material which is used for second harmonic generation. $(NH_4)_2O_5B_2O_3.8H_2O$ is monoclinic structures with the lattice parameters a=7.189 Å, b=11.308 Å, c=7.217 Å, volume=578 $Å^3$ and its relative second harmonic generation (SHG) efficiency is 0.75 times that of KDP crystal.

Recently, it has been reported that doping NLO crystals with organic impurities can alter various physical and chemical properties and doped NLO crystals may find wide applications in opto electronic devices compared to pure NLO crystals [10–12]. Since no work has been noticed in the literature on thiourea doped ammonium penta borate crystals, an attempt has been made to introduce thiourea, an organic NLO material into the lattice of $(NH_4)_2O_5B_2O_3.8H_2O$ crystal to alter its physical and chemical properties. The aim of this paper is to report solubility and growth, single crystal and powder X-ray diffraction (XRD) studies, SHG, UV–visible transmittance studies, thermo gravimetric and differential thermal analyses (TG/DTA) studies, melting point and microhardnes studies of thiourea doped ammonium penta borate single crystals.

MATERIALS AND METHODS

2.1. Crystal growth

Commercially available ammonium penta borate (AR grade), thiourea (AR grade) and double distilled water were used to grow the tilted compound by slow evaporation technique. The saturated solution of 1mol% thiourea doped ammonium penta borate (APB) was prepared at room temperature (303K) and filtered using WHATMAN filter paper (no. 1001 125). The filtered solution was tightly closed with thin plastic sheet, so that the rate of evaporation could be minimized. After the period of 28 days, colourless, transparent crystals were obtained.

2.2. Characterization analyses

The as grown single crystal of glycine barium dichloride was subjected to different characterization studies such as powder X-ray diffraction, FT-IR and UV–vis–NIR analyses. Thermal stability of the sample was tested using differential scanning calorimetry and thermo gravimetric analysis, respectively. The relative second harmonic generation has been carried out by Kurtz powder technique in order to confirm the nonlinearity of the crystal.

RESULTS AND DISCUSSION

3.1. Single crystal and powder X-ray diffraction analyses

The single crystal X-ray diffraction has been carried out using ENRAF NONIUS CAD4 diffractometer. From this measurement the lattice parameters were found and are presented in Table.1.

Table 1. Lattice parameters of thiourea doped APB crystals

S. No	Sample Name	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Volume(Å^3)
1	APB	7.189	7.189	7.217	90	90	90	578
2	Tiourea doped APB*	7.182(2)	11.306(4)	7.174(1)	90	99.94(2)	90	573.8(3)

The calculated parameters are well matched with the reported values [11]. From the table it is conformed that the dopant material does not change the basic structure of the pure ammonium pentaborate (APB) crystal. The same powder form of the specimen was subjected to powder X-ray diffraction analysis using a Rich seifert diffractometer with CuKα_(_λ= 1.5417) radiation. The sample was scanned over the range of 10–70° at a scan rate of 1° min^{-1}. The recorded spectrum is shown in Fig. 1.

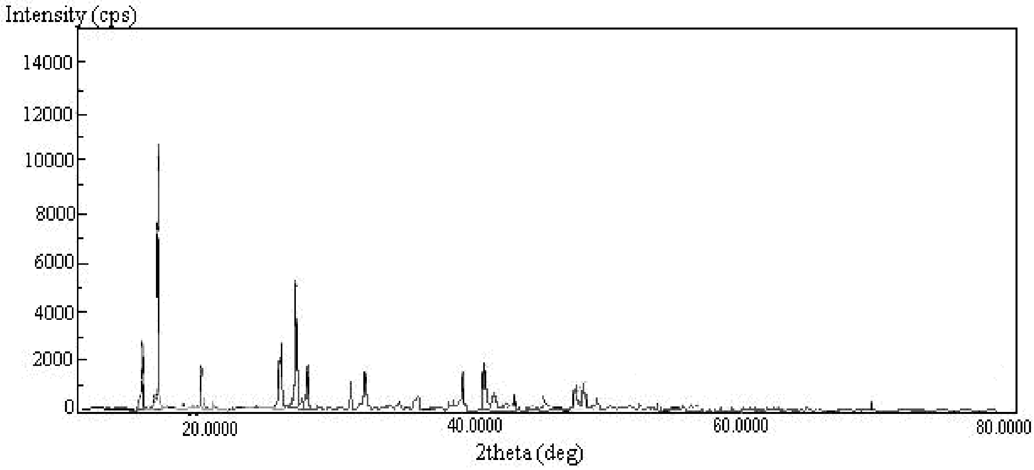

Fig. 1. Powder XRD of thiourea doped ammonium penta borate crystals.

The differences in the peak amplitude can be attributed to the different sizes and orientation of the powdered grains. Using the value of *d*, the *h k l* values of all the reflections were obtained (Table 2). The powder XRD experiment shows that the synthesized material and the grown crystals are the single phase of thiourea doped APB. The unit cell parameters have been calculated using the TREOR programme. The observed values are good in agreement with the single crystal XRD values.

Table 2. Powder XRD data for thiourea doped APB

2 theta	dobserved	dcalculated	h k l
16.24	5.4534	5.493	1 0 2
25.3	3.5173	3.529	0 0 6
27.4	3.2524	3.249	1 3 1
30.68	2.9117	2.916	2 2 1
39.1	2.3019	2.303	0 1 9
40.82	2.2088	2.206	0 4 6
48.12	1.8894	1.884	0 6 0

3.2. FTIR studies

The Fourier transform infrared spectrum of thiourea doped APB crystal was recorded on PerkinElmer FT-IR spectrophotometer using KBr pellet technique at 300K in the range of 450–4000 cm^{-1}. The FT-IR spectrum thiourea doped APB crystal is presented in Fig. 2. The very strong band absorbed at 3385 cm^{-1} is due to OH symmetric stretching vibrations. The B-O vibrations of borate crystal have their absorption bands in the frequency region 782– 1432 cm^{-1}.

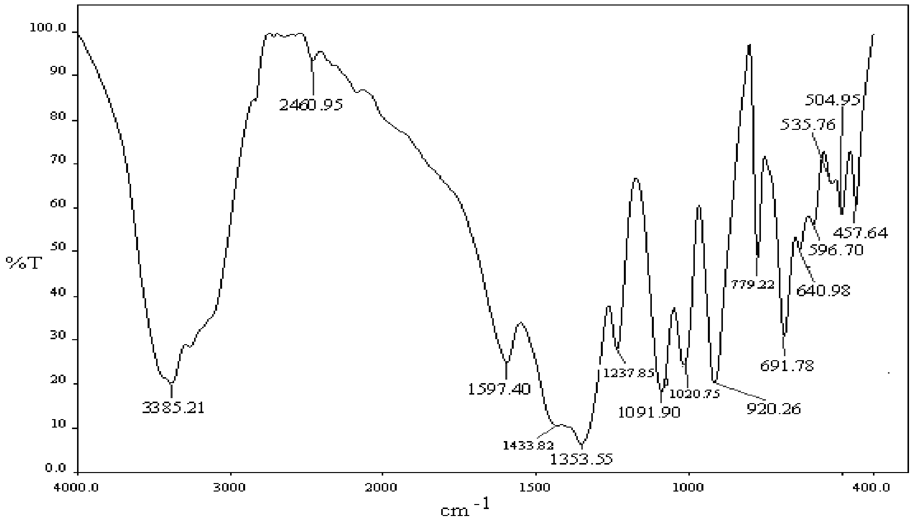

Fig. 2. **FTIR spectrum of thiourea doped ammonium penta borate crystals.**

Table. 3. Vibrational band assignments of thiourea doped APB crystal

KPB[12]	APB[9]	Thiourea doped APB*	Band assignments
3445	3435	-	(O-H) asymmetric stretching
-	3326	3385	(O-H) symmetric stretching
-	1642	1597	NH_4 asymmetric bending
1438	1432	1433	B -O terminal asymmetric stretching
-	1396	-	NH_4 symmetric bending
1356	1354	1353	B-O asymmetric stretching
1251	1244	1237	CH_2 torsion
1103	1101	1091	B-O terminal asymmetric stretching
1027	1024	1020	B-O terminal symmetric stretching
923	924	920	B-O ring stretching
784	782	779	B-O ring stretching
695	695	691	O-B-O ring asymmetric bending
591	590	596	O-B-O terminal bending
509	504	504	O-B-O ring bending

The band observed at 1597cm^{-1} is assigned to NH_4 asymmetric bending vibrations. The very strong peak at 1020 cm^{-1} is attributed to B-O terminal symmetric stretching vibration. The B-O terminal asymmetric stretching vibration is observed at 1433 cm^{-1} [13]. The vibrational frequencies with their assignments are summarized in Table. 3. Comparisons of APB and thiourea doped APB shows slight shift in absorption bands. This shift in absorption bands may be due to addition of thiourea in APB.

3.3. Optical transmission spectral analysis

To determine the transmission range and hence to know the suitability of the grown crystals for optical applications, UV-Vis analysis was made between 190 and 1100nm using Perkin Elmer Lambda 35 spectrophotometer. It covered a broad region which near ultra violet (200 to 400nm), visible (400 to 800nm) and far-infra red (800nm to 1100nm). The plot of % transmittance Vs wavelength (nm) is shown in the Fig. 3.

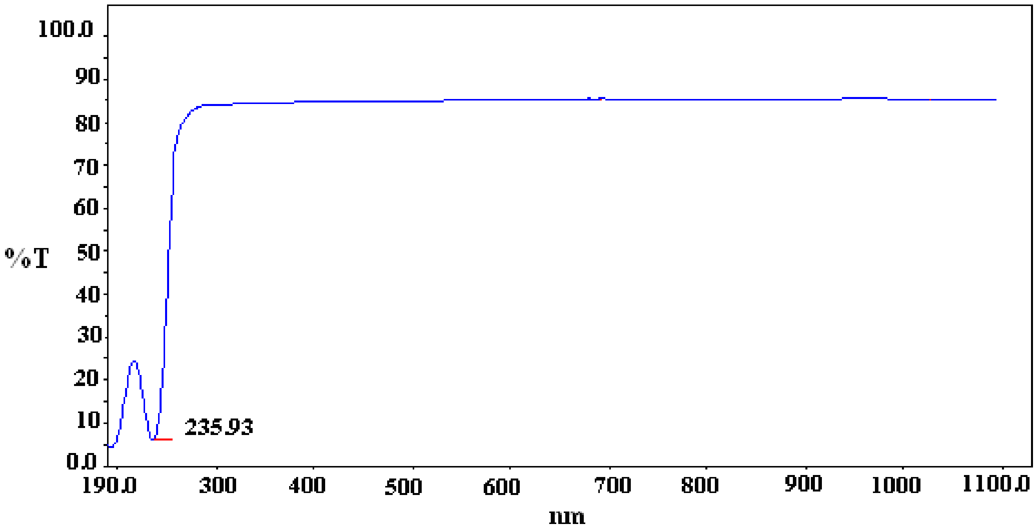

Fig. 3. UV-Vis spectrum of doped ammonium penta borate crystals.

The absorbance is not registered in the measured wavelength range starting from 235 to 1100nm. At 235.93 nm a sharp fall of transmittance to zero was observed indicating a single transition in the near UV region of thiourea doped APB. The nearly sharp fall in the transmittance at 235.93 nm suggests nearly similar distribution of energies among all molecules of thiourea doped APB single crystal. Absence of absorption in the region between 235 to 1100nm is an advantage as it is the key requirement for materials having NLO properties. [14, 15]

3.4. Second harmonic generation (SHG) measurement

Kurtz and Perry powder SHG test is an extremely useful for initial testing of materials for second harmonic generation. The fundamental beam of 1064 nm from Q switched Nd: YAG laser was used to test the second harmonic generation (SHG) property of thiourea doped APB crystal. Pulse energy 4.5 mJ/pulse and pulse width 8 ns and repetition rate 10Hz was used. The photo multiplier tube (Hamahatsu R2059) was used as detector and 90^{o} geometry was employed. The SHG signal generated in the sample was confirmed from emission of green radiation from the sample. The optical signal was converted into electrical signal by means of photomultiplier tube, the output measured for pure APB and thiourea doped APB crystals were 54 and 67mV respectively. This indicates that SHG conversion efficiency of thiourea doped APB is 1.3 times greater than that of pure APB.

3.5. Thermal analysis

Thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA) are very important characteristic techniques to identify the thermal stability of the grown crystal. TG/DTG and DTA curves were recorded for the thiourea doped APB crystal using SDT Q600 V20.5 Build15 thermal analyzer in the range of temperature from 0 and 1000°C at a heating rate of 20°C/min in nitrogen atmosphere (Fig. 4).

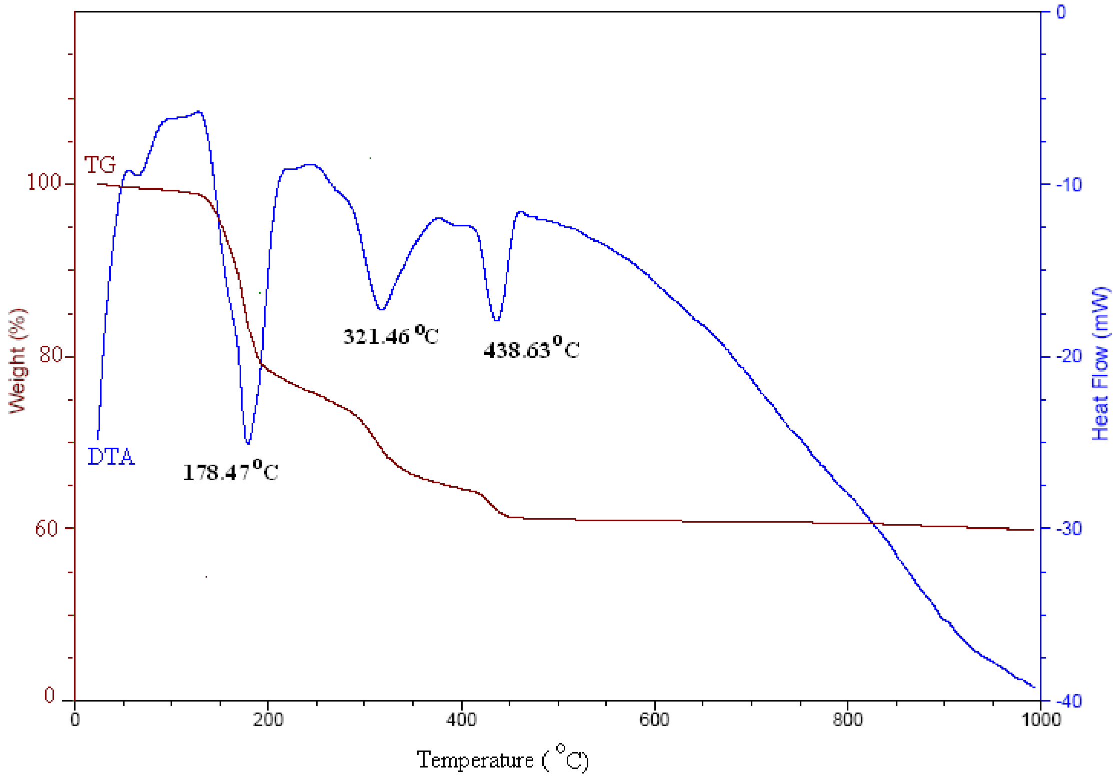

Fig. 4. TG/DTA spectrum of thiourea doped ammonium penta borate crystals

A ceramic crucible was used for heating the sample. The initial mass of the material subjected to analysis was 10.4870mg. Three weight loss steps were observed from the TGA curve. The material was stable up to 176°C and then weight loss takes place. As seen in the reaction steps the thermal decomposition of APB [16] takes place in three steps: dehydration, decomposition and deammination (removal of ammonia). In the first step of decomposition three water molecules were removed. The second step of weight loss takes place between the temperature 288°C and 336°C. In the second stage of weight loss another two water molecules takes place. These two water molecules are difficult to remove during dehydration and can only be removed by decomposition. Third step of decomposition is observed between the temperature 412°C and 443°C. During this stage of decomposition one ammonia molecule is removed. The DTA curve clearly follows the TG curve except a very small defused peak appears at 67°C and can be neglected. Sharp and well resolved peak is observed at 178.47°C as the second endothermic which is due to the decomposition of another two molecule. Third endothermic peak is observed at 321.46°C and corresponds to the loss of two water molecules present in the crystal lattice. The fourth endothermic peak is observed at 438.63°C which is related to the removal of ammonia molecule.

3.6. Differential scanning calorimetry

Differential scanning calorimetric study (DSC) was carried out on a DSC Q20 V24.2 Build 107 calorimeter with a heating rate of 10°C/min in nitrogen atmosphere. For this a small piece of crystal weighing 2.5000 mg was placed in an aluminium pan. The sample was canned over the temperature range from 0 to 500°C. The DSC plot [Fig. 5] shows a sharp peak at 175.12°C. This well marked endothermic peak is due to the melting of the compound.

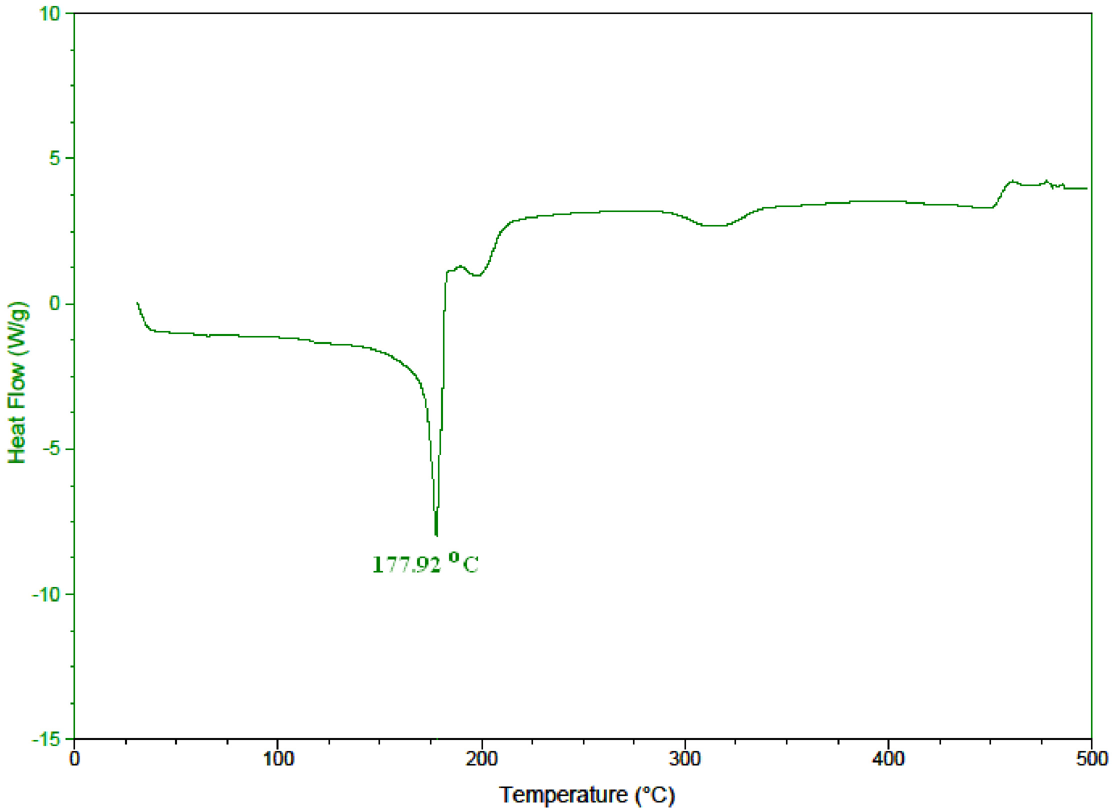

Fig. 5. DSC spectrum of doped ammonium penta borate crystals.

CONCLUSION

The 1 mol% thiourea doped APB crystal has been grown from aqueous solution by low temperature solution growth, slow evaporation technique. The Kurtz and Perry powder SHG test shows that the SHG efficiency of 1 mol% thiourea doped APB is 1.3 times more than pure APB. The FTIR spectrum confirms the presence of all the functional group and presence of thiourea in the grown crystal. The powder and single crystal X-ray analysis confirms the monoclinic structure of the grown crystal. UV–visible study reveals the thiourea doped APB crystal has lower cutoff wavelength at around 235 nm. The thermo gravimetric analysis and Differential Scanning Calorimetry showed the crystal is thermally stable up to 178^{o}C temperature.

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