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Investigation of Structural, Spectral, Optical and Thermal properties in Grown Pure Bis Thiourea Zinc Acetate (BTZA)

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Abstract: *The nonlinear optical single crystal of bisthiourea zinc acetate (BTZA) was grown successfully by slow evaporation technique using water as solvent at room temperature. The lattice parameters of the grown crystal were determined by X-ray diffraction studies. The quality of the grown crystal was examined by scanning electron microscopy (SEM).The optical transparency was determined by UV-visible and photoluminescence spectroscopy studies. The thermal behavior of the grown crystal was investigated by DTA and TGA analysis. The presence of functional group was studied using FTIR spectra. The second harmonic generation (SHG) of BTZA was confirmed the nonlinear property of the crystal by Kurtz powder technique.*
Keywords: *Crystal Growth, Second Harmonic Generation, FT-IR, TGA/DTA.*

I. Introduction

Non linear optical (NLO) materials play an important role in the field of fiber optic communication, laser technology and optical signal processing. They are also used in the area of optoelectronics, telecommunication and optical storage device [1] due to their potential applications in emerging optoelectronic technologies [2,3,4,5,6]. Single crystals of the inorganic complex of thiourea have evoked much interest in the last few years due to their non linear optical properties [7,8,9,10]. Thiourea is an organic matrix modifier due to its large dipolmoment and its ability to form extensive network of hydrogen bonds [11]. The centrosymmetric thiourea molecule, when combined with inorganic salts yields non centrosymmetric complexes, which has nonlinear optical properties. Metal complexes of thiourea, commonly called semiorganics, include the advantages of both organic and inorganic part of the complex [12]. The structural and the optical, mechanical and thermal properties have been reported in detail in the literature (Jayalakshmi and Kumar 2006; Kannan et al 2004; Lydia Caroline and Vasudevan 2009; Thomas Joseph Prakash and Ruby Nirmala 2010). In this work, we discuss the synthesis and growth of BTZA single crystal and its structural, optical and thermal characterization.

II. Experimental Details

A. Crystal growth

BTZA salt was synthesized by using zinc acetate and thiourea in the stoichmetric ratio 1:2.The calculated amount of salt was dissolved in double distilled water and stirred well for 3 hours to yield a homogenious solution using magnetic stirrer. The purity of BTZA is achieved by successive recrystallisation. The solution was slightly heated up to an optimum temperature of 50°c to avoid decomposition of the solute molecules. The prepared solution was allowed to dry at room temperature and good optically transparent crystals were obtained by slow evaporation technique in a period of 25 days. The photograph of the crystal is shown in the figure 1.

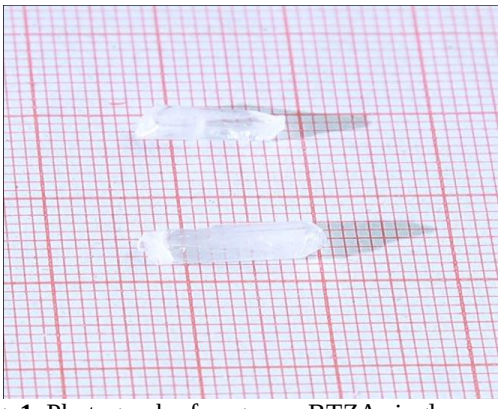

Fig. 1. Photograph of as grown BTZA single crystal

III. Results And Discussion

B. Single XRD

Single XRD is a non destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions and bond length. Single crystal XRD studies were carried out using Bruker Kappa Apex II diffractometer. The single XRD analysis shows that the crystal belongs to monoclinic system with space group P_{21}/n. The unit cell dimensions are a = 7.1270 A˚,b = 17.7232 A˚,c = 11.1827 A˚,α==90°,β=103.096°,γ=90°.The PLATON diagram of as grown BTZA single crystal is shown in figure 2.

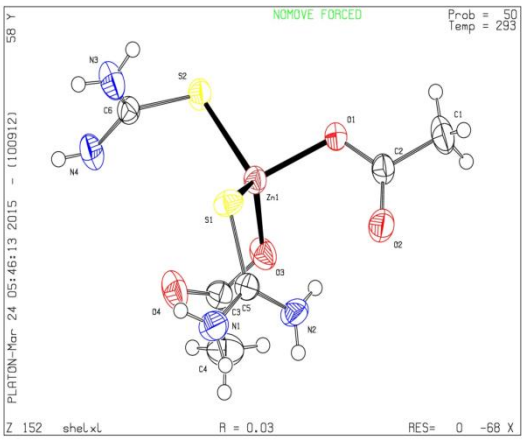

Fig. 2. The PLATON diagram of BTZA

Table 1. Crystallographic parameters

Chemical formula	Zn (NH2CSNH2)2(CH3COO)2
Cell Parameters	a = 7.1270 A˚ b = 17.7232 A˚ c = 11.1827 A˚
Volume	1375.79(12) A^3
Molecular Weight	335.7
System	Monoclinic
Space group	P21/n

C. Powder XRD

Powder XRD provides most definite structural information. The structural characteristics were done by X-ray powder diffraction method, using Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ=1.5406 Å, X-ray tube voltage = 40 kV and current = 35 mA). The scan was taken in the 2θ range from 0 - 80^0 at increments of 0.02° with a step time of 65.5 s. The powder x ray diffraction results are shown in the figure 3.

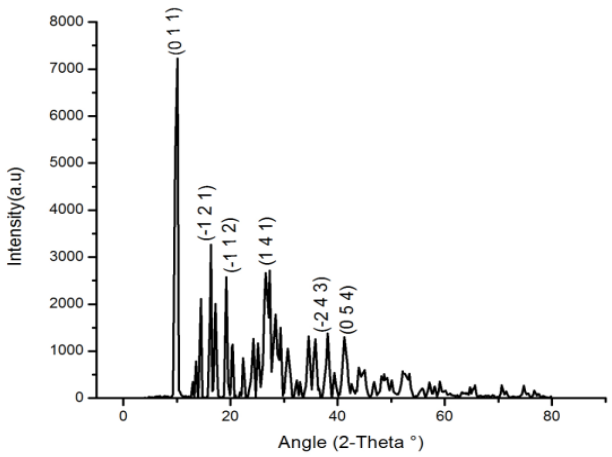

Fig. 3. Powder X-ray diffraction pattern of BTZA

D. Scanning electron microscopy

The surface morphology of samples were analyzed with a scanning electron microscope JEOL MODEL JSM-6390LV, operating at 20 kV. The SEM photographs are shown in figure 4. SEM images shows the pebble like structure of the crystal which is due to the surface roughness [21]

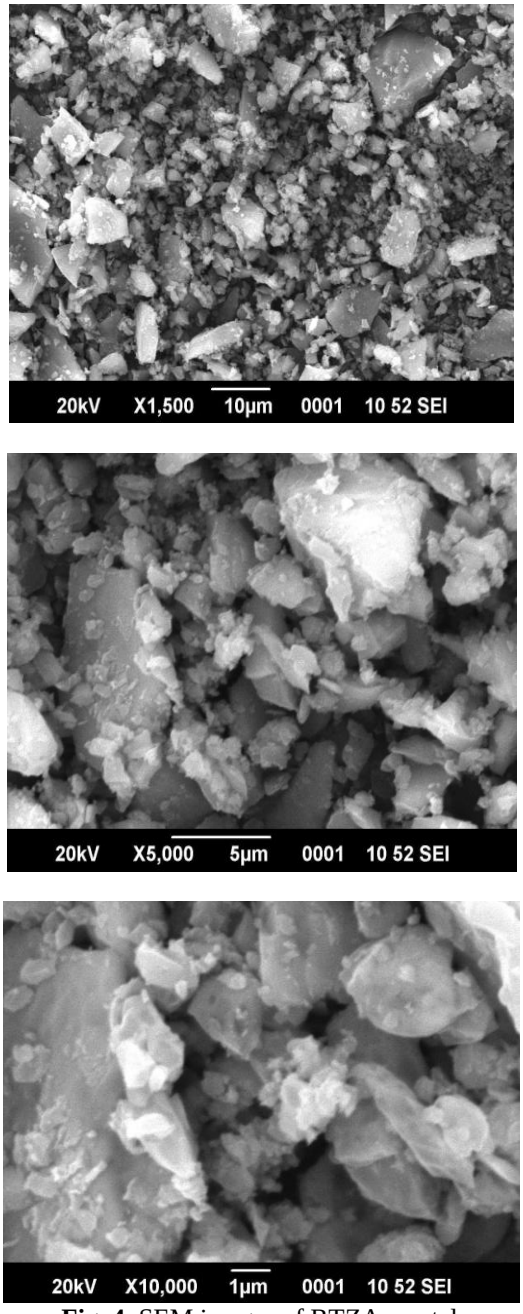

Fig. 4. SEM images of BTZA crystal

E. U V –Vis Spectroscopy

The optical absorbance was recorded from uv visible in the wavelength range of 200-1200 nm using UV–Visible spectrophotometer (Varian, Cary 5000). The thickness of the sample used for measurement was 2mm.The recorded spectra is shown in the figure 5. The absorbance was reduced drastically between the wavelength of 360 nm and 1200nm offering wide transmission range. The wide range of transparency of grown crystal is an added advantage in the field of optoelectronic application [16].

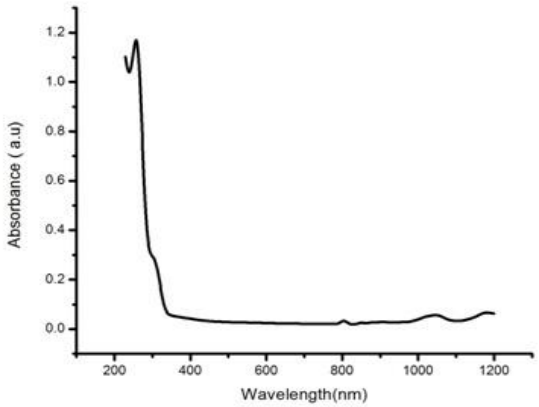

Fig. 5. UV-Vis spectrum of BTZA

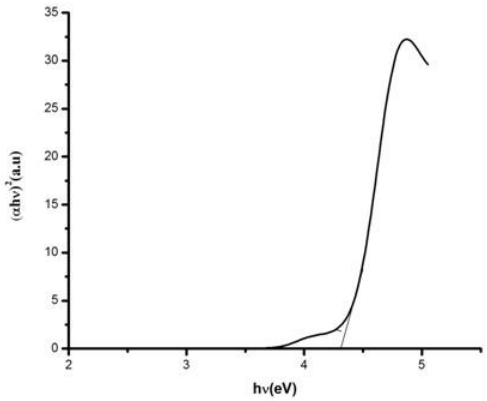

Fig. 6. $(\alpha h\nu)^2$ versus photon energy (hν) of BTZA

The optical bandgap (E_g) can be evaluated from the transmission spectra [13] using the relation $\alpha h\nu = A (h\nu - Eg)^{1/2}$, where A is a constant, E_g the optical band gap ,h the Planck's constant. The optical band gap of BTZA crystal is found to be 4.3eV and is shown in the figure 6. The lower absorption and high optical band gap is most desirable for UV tunable laser materials [13].

F. Photoluminescence Studies

The photoluminescence (PL) spectrum of the sample was recorded by fluorescence spectrometer, Perkin Elmer-LS 55, using an excitation wavelength of 275 nm is shown in the figure 7.The high energy violet emission was observed at 436nm corresponding to an energy of 2.84 eV.

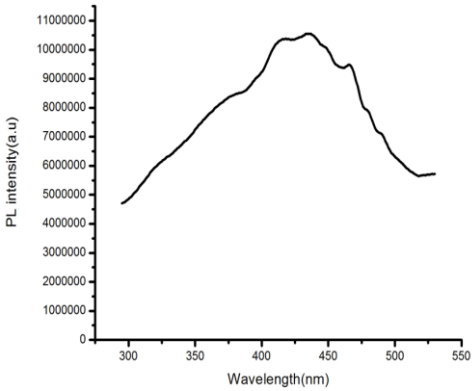

Fig. 7. Photoluminescence spectrum of BTZA

The two blue emissions were observed at 465 nm(2.66 eV) and 479 nm (2.58 eV) which is suitable for photonic device applications. Peaks in the visible region can be assigned to lattice related processes [23].

G. Thermal studies

Thermal behavior of the sample was analyzed by thermo gravimetric analyzer (TGA) and differential thermal analyzer (DTA) using Perkin Elmer STA 6000, heating from ambient to 700 °_C at a rate 10 °C/min is recorded and shown in the figure 8. There is no weight loss below 150°C due to the absence of water in the crystal structure. The weight loss of about 57 % takes place in the region 187^{o} C to 280^{o}C. The weight loss may be due to decomposition of the compound and organic compound evaporation. In DTA curve there is an endothermic peak at 187.48^{o}C, which is the melting point of the specimen. No decomposition up to the melting point ensures the suitability of the material for the application in lasers where the crystals are required to withstand high temperature. The analysis also shows that BTZA is thermally stable up to 150^{0}C; hence it is suitable for NLO applications.

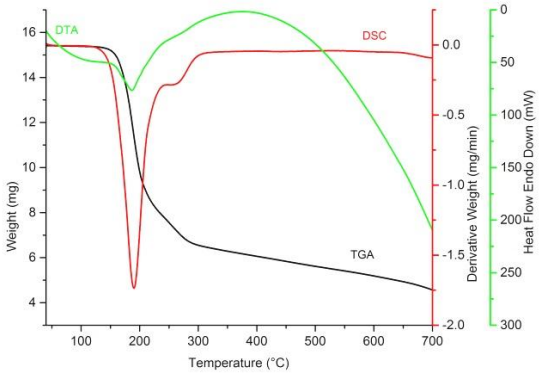

Fig. 8. TG/DTA/DSC curves of BTZA

H. NLO studies

The non linear optical property of the grown crystal was determined using Kurtz and Perry method. A high intensity Q-switched mode locked Nd-YAG laser was used to generate about 1.13 mJ/pulse at the 1064 nm fundamental radiation. The input laser beam with pulse duration 10 ns and frequency repetition 10 Hz is passed through the micro crystalline powdered sample packed in a capillary tube. The efficiency of the sample was compared with the micro crystalline powder of KDP as the reference material. The bride green emission (532 nm) from the specimen was collected a photomultiplier tube and finally measured on the storage oscilloscope (CRO) as output voltage. The output from the SHG test confirms the non linear nature of the crystal.

I. FTIR

Fourier transform infrared (FTIR) spectra of the samples were recorded by FTIR spectrophotometer (Thermo Nicolet, Avatar 370) in the range 4000 to 400cm^{-1} by KBr pellet technique [22]. The recorded FT-IR spectra of undoped BTZA is provided in figure 9.

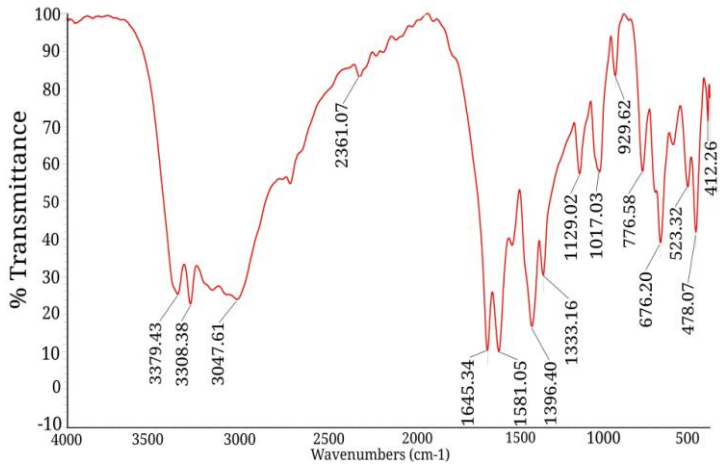

Fig. 9. FT-IR spectrum of BTZA crystal

In BTZA, Zinc can coordinate with thiourea in two possible ways that is through nitrogen or through sulphur of thiourea [14]. The high frequency N-H absorption bands in the region 3100- 3400cm^{-1} in the spectrum of thiourea were not shifted to lower frequencies on the formation of metal thiourea complex indicating that nitrogen to zinc bonds are absent and that bonding must be between sulphur and zinc atoms [15]. The S-C-N bending vibrations at 494 cm^{-1} of thiourea shifted to lower frequency 478 cm^{-1}. The symmetric and asymmetric C=S stretching vibrations at 730 and 1417 cm^{-1} of thiourea are shifted to low frequency region at 676 and 1396 cm^{-1} in BTZA respectively which confirms the formation of metal sulphur coordination bond [19]. C=S stretching vibration at 1089 cm-^{1} is shifted to higher frequency 1129 cm^{-1}.This shows that binding of zinc with thiourea is through sulphur [20]. It can be seen from Table 2.

Table 2. FTIR Data Comparison of BTZA with thiourea

Thiourea(cm-1)	BTZA (cm^{-1})	Assignment
494	478	S-C-N symmetric bending
730	676	C=S symmetric stretching
1089	1129	C=S asymmetric stretching
1417	1396	C=S asymmetric stretching
1627	1645	NH_2bending

The observed bands of BTZA with their vibrational assignments have been tabulated in Table 3 along with the reported values of BTZA for comparison.

Table 3. Single crystal data of pure BTZA crystals

BTZA cm^{-1}(reported[17])	BTZA cm^{-1}	Assignment
487	478	S-C-N symmetric bending
777	776	C=S symmetric stretching
1135	1129	C=S symmetric stretching
1403	1396	C=S asymmetric stretching
1582	1581	NH_2bending
3375	3379	NH_2 stretching

IV. Conclusion

Good quality single crystal of BTZA was grown by slow evaporation technique under room temperature. Grown crystals were characterized by XRD and confirmed that the crystal belongs to monoclinic system with space group P_{21}/n . Optical transmission study confirms the quality of the crystals for NLO application. The optical band gap was found to be 4.3eV. The photoluminescence studies confirms the quality of the crystals for photonic device applications. TGA and DTA analysis has revealed that BTZA is stable up to 150^{o}C, after that it undergoes a physical transformation associated with mass changes. The functional groups were verified using FTIR analysis. SHG conversion efficiency makes the crystal a latent material for NLO application.

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