Scientific Journal of Impact Factor (SJIF): 5.71
e-ISSN (O): 2348-4470
p-ISSN (P): 2348-6406

International Journal of Advance Engineering and Research Development

International Conference on Momentous Role of Nanomaterials in Renewable Energy Devices

Volume 5, Special Issue 07, April-2018 (UGC Approved)

Synthesis, Growth and Characterization of Nonlinear optical material Bis Thiourea Zinc (BTZA) Acetate Single Crystals by Slow Evaporation Method

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Abstract - *A semi organic nonlinear optical crystal of Bis thiourea Zinc acetate (BTZA) has grown by slow evaporation technique.The raw material for the growth of BTZA was synthesized by 1:2 molar ratio in de-ionized water. The crystal system and lattice parameters determined from X-ray diffraction. Fourier transform infrared studies confirm the various functional group present in the grown crystal. The UV-Visible spectrum absorbance and transmittance was recorded in the wavelength range of 190–1100 nm. The absorption reveals that the lower cutoff wavelength is 230nm. The thermal behavior of the grown crystal and noncentrosymmetric space group. The second harmonic generation efficiency of the complex was studied using the Powder Kurtz method and was found to be 1.2 times greater than that of KDP. The EDAX Spectrum to be analysis of complex variable is determined to be BTZA crystal.*

KeyWords: *FTIR, UV-Visible, Vicker's hardness test, Powder XRD, Single XRD, TGA-DSC analysis, EDAX, SHG efficiency measurement.*

I. INTRODUCTION

Now a days nonlinear optical materials have various area of telecommunications and optical storage devices. The NLO crystals have been found to perform many applications in optical communications, optical information processing, optical computing high density data storage and laser fusion recations [1-6]. In second order nonlinear optical materials have recently attracted of their potential applications in emerging optoelectronic devices. The inorganic NLO materials like KDP, ADP, L-arginine and L-arginine phosphate, Bisthiourea Zinc acetate, L-histidinium tetrafluroborate, L-histidinium tetrafluroborate have gained significant attention in the last few years[7-9]. In the present work the title compound was successfully synthesized by Bisthiourea Zinc acetate in equimolar ratio. The single crystal has been grown by slow evaporation solution growth technique using water as the solvent. The number of studies are available on the structural/ crystalline perfection. Mechanical and optical behavior of the present compound[10-16]. In view of NLO applications these studies were carried by XRD, Vickers microhardness. The grown crystals are PXRD,FTIR,UV-Visible, refractive index, and SHG measurements and electrical studies were discussed. These studies show high efficiency in NLO single crystals.

II. EXPERIMENTAL

A. Crystal growth

BTZA single crystals were synthesized using thiourea and Zinc acetate in deionized water by stoichiometric ratio 1:2 of the chemical recation.

$$\mathbf{2[CS(NH_2)_2] + Zn(CH_3COO)_2 \longrightarrow Zn[CS(NH_2)_2(CH_3COO)_2}$$

The solution was stirred using magnetic stirrer and the mixture was heated upto 50°C to decomposition of the solute molecules. The thiourea coordinating from different phases of metal-thiourea complexes, purity of synthesized salt was improved by recrystallization process. The single crystal pure of BTZA was harvested in a period of 30 to 40 days of grown crystal.

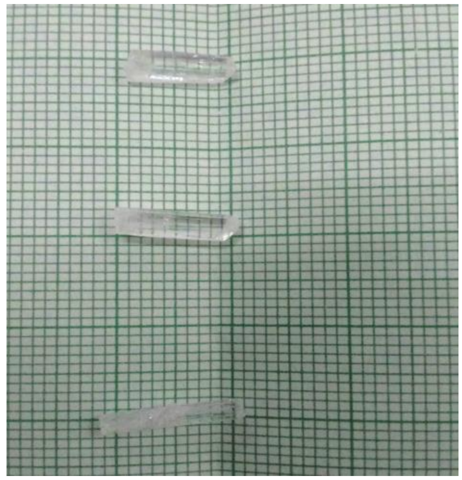

Figure 1: The Photograph of BTZA Single crystal

III. CHARACTERIZATION

A. Single Crystal X-Ray diffraction Analysis

The single crystal X-Ray diffraction has been using Bruker D8 venture diffractometer. The unit cell parameters in determined by APEX2 program. The single crystal diffraction analysis of pure BTZA single crystal reveal that the compound crystallizes **Powder** in monoclinic system. The lattice parameters for pure BTZA are a=7.17 Å, b=17.80 Å, c=11.23 Å and α=γ=90˚, β=103.21˚ and cell volume V=1396Å^3 respectively.

B. X-Ray Diffraction Analysis

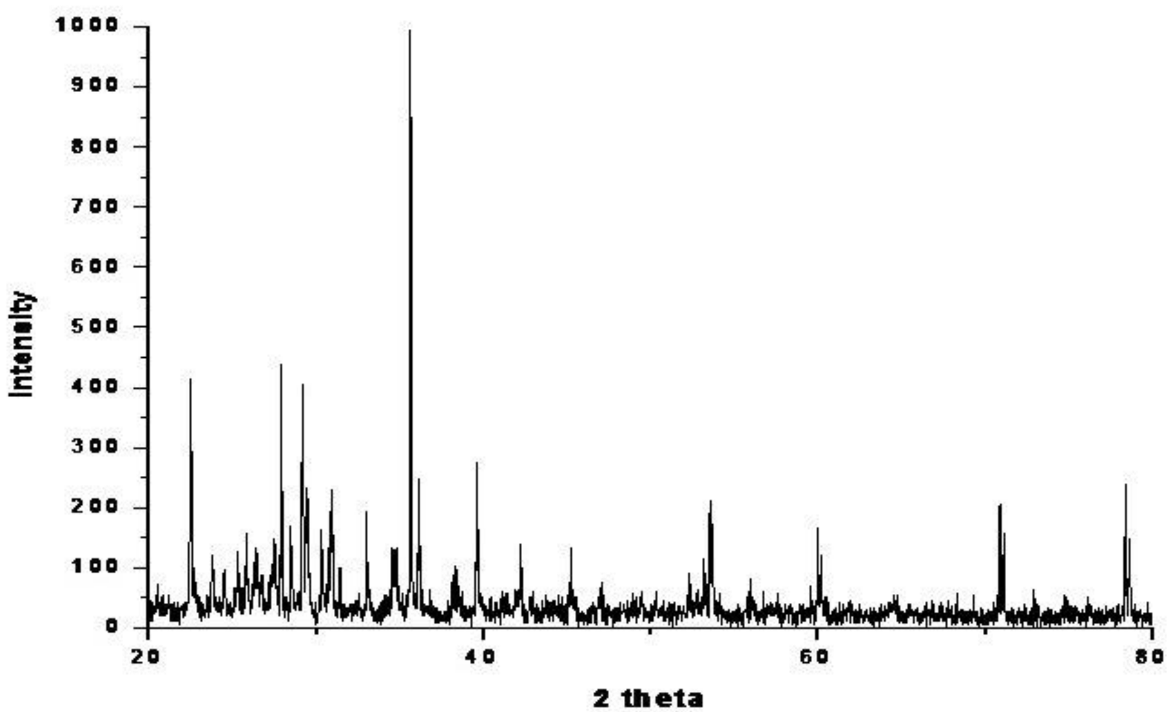

Figure 2. Powder X-ray diffraction pattern of pure BTZA crystal

The sample of the grown crystal was subjected to powder X-ray diffraction analysis using analytical. Xpert PRO powder X-ray diffractrometer employing CuKα radiation (λ=1.5405Å). the XRD pattern of pure BTZA crystal shown in figure.2. the observed peaks in spectrum indicated the resemblance of grown crystal to monoclinic structure. The evaluated cell parameters are a=14.431 Å, b=5.340 Å, c=10.981 Å. and α=γ=90˚, β=103.37˚ respectively.

C. FTIR Analysis

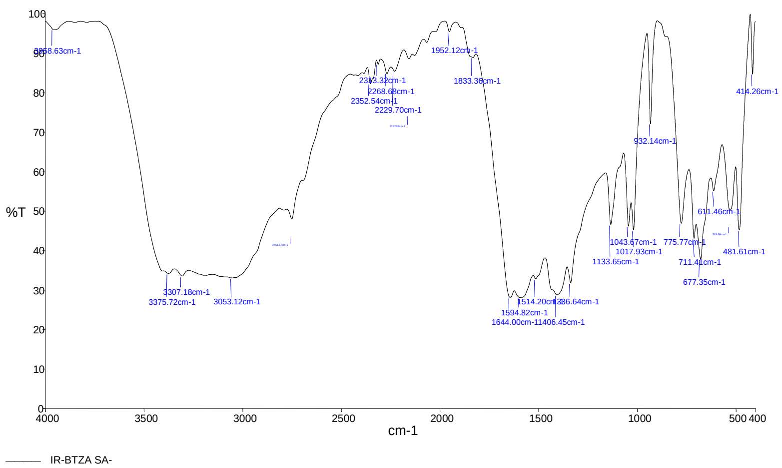

Figure 3. FTIR Analysis of BTZA Single Crystal

The infrared spectroscopy used to identify the functional groups of the samples FTIR spectra of pure BTZA single crystals were recorded in the KBr pellet technique. The frequency region from 400-4000 cm^{-1} ranges using perkin elmer spectrometer. The FTIR spectra comparision of the grown crystals is shown in the table1 & figure 2. The FTIR spectrum of pure BTZA with the spectra of thiourea a shift in the peak was observed, the confirmed metal coordination with thiourea. The N-H vibration bands in the high frequency range from 3000-3400cm^{-1}. It indicates that the bonding is between sulphur and zinc atoms, the peaks at 2751cm^{-1} for pure BTZA and the band 1644cm^{-1} which are assigned C=N stretching vibration. The appearance of peak 1406 and 1043cm^{-1} for pure BTZA single crystals. In absorption of pure C-S and C-N strectching frequency of complex formation. In pure BTZA single crystals of symmetric and asymmetric vibrations at 932 and 775cm^{-1} respectively. The FTIR studies shows that in the spectra BTZA is a frequency band in the lower frequency band in the lower frequency region of BTZA single crystals.

Table 1. FTIR data of Pure BTZA single crystal

Pure BTZA Wavenumber (cm^{-1})	Assignment
3375	N-H Stretching
2751	C-H Stretching
1644	C-N Stretching
1406	Asymmetric C=S Stretching
1043	C-N Stretching
932	C-O-H Bending
775	Symmetric C=S Stretching

D. UV-Visible analysis

The UV-Vis spectrum of pure BTZA single crystal was recorded in the range of 200-1100nm. The instrument used was LAMBDA-35 UV-Vis spectrophotometer. The optical study for SHG, the material is good transparent in the wavelength region for NLO material. The transmittance is found to be maximum in the visible near infrared region.

In pure BTZA single crystal is found to be 80% transmittance wavelength. The lower cutoff frequency was at 270nm in pure BTZA single crystals for the opto electronic applications.

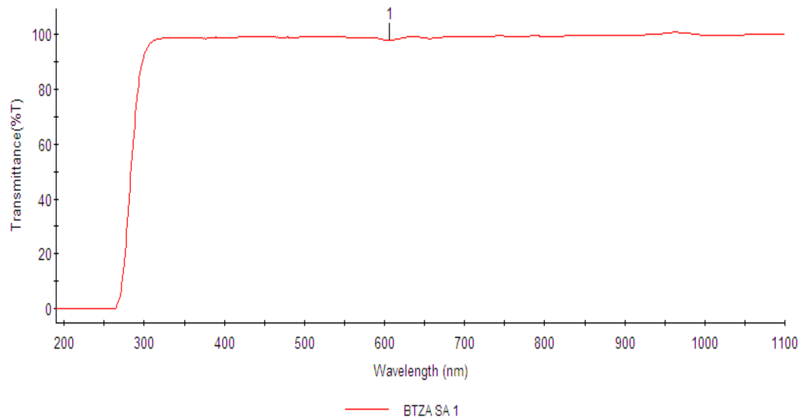

Figure 4. UV-Visible transmittance of BTZA Crystal

E. Microhardness measurement

Vickers microhardness test is used to hardness of the material. The hardness number has to be evaluated of the load applied and the cross-sectional area of the depth of the impression. The Smooth surfaces of a grown pure BTZA crystals. The Vickers hardness value is calculated from the formula:

$H_v = 1.8544*(p/d^2)$ kg/mm^2

Where p is the applied load in kg and d is the average diagonal length in millimeters of the impressions in the present study. The Vickers hardness was measured using Leitz-Wetzler hardness tester in different load is shown in fig.5. it is observed that the microhardness increases with the increase of load at lower values to the work hardness of the surface layers. At higher loads 100g the microhardness shows a tendency to surface.

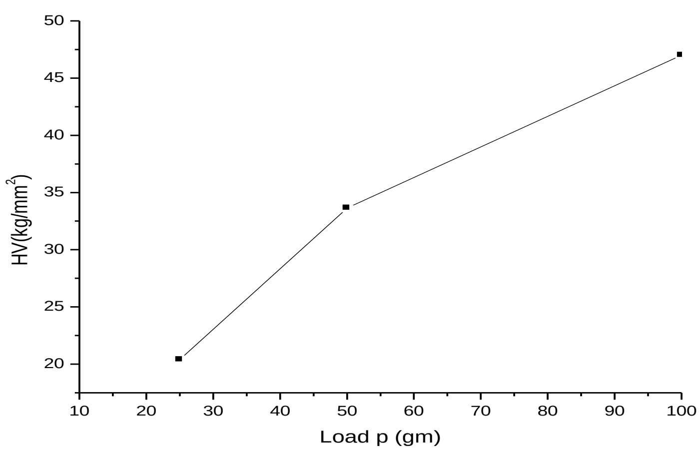

Figure 5. Hardness Vs load graph of pure BTZA crystals

F. EDAX Analysis

Energy dispersive X-ray analysis for characterizating the elements was present in the grown crystal. EDAX analysis carried out using JEOL-6360 scanning electron microscope. The recorded sepectrum is shown fig.6. The presence of carbon, nitrogen, nickel, oxygen, slphur and zinc elements show incorporation of Pure BTZA grown crystal.

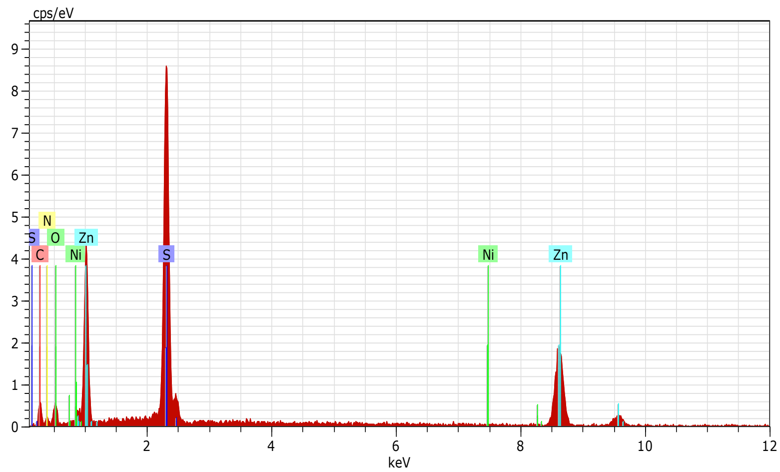

Figure 6. EDAX spectrum of pure BTZA crystal

G. Thermal Analysis

TGA/DSC

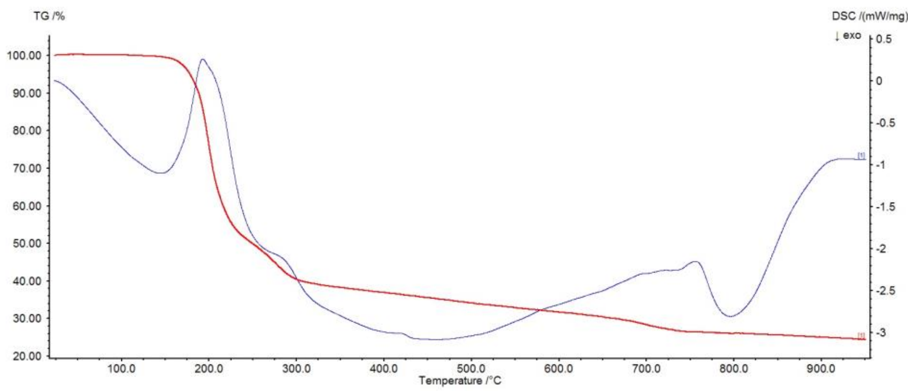

Figure 7. Thermal analysis of TGA/DSC pure BTZA crystal

The thermal stability and physicochemical changes of BTZA single crystal were studied by thermo gravimetric analysis and differential scanning calorimetric analysis. The curve of BTZA shown in fig.7. TGA/DSC. The thermal decomposition starts at 199.2˚C the acetate complexes with inorganic ligends the decomposition of thiourea molecules and the decomposition of the Zinc acetate and metal oxides. The thermal decomposition of BTZA is exothermic peak at 200˚C in the DSC analysis shows the melting point of the complex on compared to other thiourea based complex 250˚C and the allythiourea metal halides to be thermal stability of the BTZA good quality in single crystal.

H. SHG efficiency measurement

The grown crystals were subjected to the NLO study to measure the efficiency with pure BTZA single crystal. The SHG Property of the grown crystal was tested by the Kurtz Perry powder method. The fundamental beam of wave length 1064nm from a Q-Switched Nd:YAG laser with a pulse energy 1.5mJ/Pulse, the pulse width 6ns and repetition rate 10Hz was used. From the output Power Measurement, the SHG efficiency of Pure BTZA was found to be 1.2 times greater than of KDP.

IV. CONCLUSIONS

Pure BTZA single crystal were grown by solution growth method at room temperature. The single crystal analysis of lattice parameter to be calculated. The powder X-Ray Diffraction were indexed of monoclinic system. The FTIR confirmed to be analysis of functional group of grown crystal. UV-visible to be analysis of the transmittance is found to be maximum in the visible near infrared region in Pure BTZA crystal at the lower cutoff wavelength region in 270nm. The Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. Hardness measurement also shows that harder than pure BTZA crystals. The EDAX Spectrum to be analysis of complex variable is determined to be BTZA crystal. The TGA/DSC analysis of the allythiourea metal halides to be thermal stability of the pure BTZA crystal. The thermal decomposition of BTZA is exothermic peak at 200˚C in the DSC analysis shows the melting point of the complex on compared to other thiourea based complex 250˚C and the allythiourea metal halides to be thermal stability of the pure BTZA good quality in single crystal. The SHG was observed using a Q-switched Nd:YAG laser and its efficiency were found to be better than KDP. In Pure BTZA single crystal, a potential material for photonic device applications in future.

ACKNOWLEDGMENTS

The authors thank Dr. Sudhadevi, Sophisticated Analytical Instrumentation Facilities, Indian Institute of Technology, Chennai, for his help in cell parameter collections. The authors are grateful to Prof. G.V. Vijayaraghavan B.S. Abdur Rahman Crescent Institute of Science and Technology for extending the facilities to measure SHG efficiency. Also we thank the authorities of St. Joseph's College, Trichy for providing instrumental facility for characterization.

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