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Growth and characterization of pure and Ferrous sulphate doped Bis thiourea zinc chloride

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ABSTRACT
Non linear optical material has wide applications in the area of optical devices. That device mainly used to measure electromagnetic radiation. Single crystals of pure Bis thiourea Zinc chloride and Ferrous sulphate doped Bis thiourea Zinc chloride were grown by slow evaporation technique. The grown crystals have been subjected to powder X-ray diffraction to determine the crystalline size and unit cell parameter. The incorporation of ferrous sulphate in BTZC was confirmed by the EDAX and FTIR analysis. UV-Visible spectrum shows that the grown crystals have wide optical transparency in the entire visible region. The thermo gravimetric analysis suggests that incorporation of ferrous sulphate in the BTZC decreases the thermal stability of the grown crystal.
Key words – BTZC crystal, doping, EDAX, FTIR, UV, NLO material.

I. INTRODUCTION

Non linear optical materials play an important role in the field of telecommunication, optical switching and optical processing, optical disk data storage, laser fusion reaction, optical rectification, and in particular they have a great impact on information technology and industrial applications [1, 6]. The approach of combining the high nonlinear optical coefficient of the organic molecules with the excellent physical properties of the inorganic was found to be extremely successful in the recent past [7-11]. Thiourea which is centrosymmetric, yields excellent noncentrosymmetric materials. Thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment, and ability to form extensive network for hydrogen bond forms semi-organic compounds having low cut off wavelength and applications for high power frequency conversion.[2] The nonlinear responses induced in various molecules in solution and solids are of great interest in many fields of research[1,6]. Inorganic and semi organic nonlinear optical material have higher optical quality, larger nonlinearity, good mechanical hardness and low angular sensitivity, good mechanical hardness and low angular sensitivity when compared to organic NLO materials[12].

Some intuitive understanding of the advantages of NLO properties of thiourea co-ordination compound was found in literature [13-15]. Some of the examples of these complexes are Zinc thiourea sulphate (ZTS), Zinc thiourea chloride (ZTC), Bis thiourea cadmium chloride (BTCC), Copper thiourea chloride (CTC), and Cadmium thiourea acetate. All these crystals posses higher nonlinearity than KDP, higher laser damage threshold, polarizability and wide spectral transmission window, hence may be used for various NLO application such as electro optic modulation, optical data storage and frequency conversion application [16-23].

Zinc thiourea chloride is a potential semi organic nonlinear optical material and crystallizes in the non-centrosymmetric orthorhombic structure. Ferrous sulphate doped BTZC crystal prepared by slow evaporation growth method. The grown crystal was subjected to optical, structural and thermal characterization to study its possible use in optoelectronic and laser based application [24]. The powder X-ray diffraction confirmed the orthorhombic structure. The incorporation of ferrous sulphate in BTZC crystal bonding was confirmed by EDAX and FTIR spectra. The UV–Visible absorption spectrum was obtained to observe the change in the optical absorption spectrum was obtained to observe the change in the optical absorption of BTZC crystal after addition of ferrous sulphate. The thermal study of grown crystal was carried out using the thermo gravimetric analysis (TGA).

II. EXPERIMENTAL

Ferrous sulphate doped Bis thiourea zinc chloride crystals have been prepared by slow evaporation technique.

The BTZC salt was synthesized by dissolving zinc chloride and thiourea in the ratio 1:2 in deionized water. Single crystals of BTZC and Ferrous sulphate doped BTZC were grown employing slow evaporation techniques. The solution was stirred with magnetic stirrer at room temperature. The required quality of zinc chloride and thiourea was estimated from the following reaction.

$$ZnCl_2 + 2[CS\ (NH_2)_2] \longrightarrow Zn\ [CS\ (NH_2)_2]_2Cl_2$$

The calculated amount of salt was dissolved in the deionised water by constant stirring till super saturation stage was achieved. The purity of the synthesized salt was increased by successive recrystallization process. After 30 days a well defined transparent colorless BTZC crystal was harvested. For the growth of Ferrous sulphate doped BTZC single crystals with good transparency were harvested in 30 days. The photograph of the grown crystals is shown in figure1&2.

Fig; 1. The photograph of BTZC

Fig; 2. The photograph of Ferrous sulphate doped BTZC

III. RESULT AND DISCUSSION

The structural and optical behavior of the grown crystals were examined by powder X-ray diffraction, and thermal properties EDAX, FTIR, UV–Visible studies respectively.

3.1 Powder X-ray diffraction analysis

The powder X-ray diffraction of grown Ferrous sulphate doped BTZC crystal was carried out by using the powder X-ray diffractometer employing CuKα radiation (λ=1.5406 A^o). Using stimulated hkl values and experimental d values, The Bragg's reflection in the powder XRD patterns were indexed for pure and Ferrous sulphate doped BTZC crystals. It is observed that the relative intensities have been changed and a slight shift in the peak position was observed as a result of doping. The most prominent peaks with maximum intensity of the XRD patterns of pure and doped specimens are quite different. The observations could be attributed to strain in the lattices. Appearance of sharp and strong peaks confirms the good Crystallinity of the grown sample. The prominent well resolved Bragg's peak at specific 2θ angle reveals the high perfection of the grown crystal. The observed values are in good agreement with the reported values. When comparing the pure and Ferrous sulphate in BTZC crystal powder XRD pattern there is sharp and large peaks are appeared in the FeSO4 doped XRD of BTZC crystals. The average crystalline size Ferrous sulphate doped BTZC crystal are found to be 38.4789×10^{-9}m.

Table-1: XRD parameters of Bis thiourea Zinc chloride

2Theta	FWHM	Size	Plane
13.854	0.172	48.6287	111
15.512	0.118	71.0232	200
27.611	0.166	51.4994	111

Table-2: XRD parameters of Ferrous sulphate doped Bis thiourea Zinc chloride

2Theta	FWHM	Size	Plane
13.634	0.181	46.1934	111
15.254	0.190	44.0975	200
16.541	0.209	40.1487	002
19.500	0.273	30.8579	002
20.362	0.269	31.3564	111
27.332	0.231	36.9901	111
54.279	0.235	39.7083	002

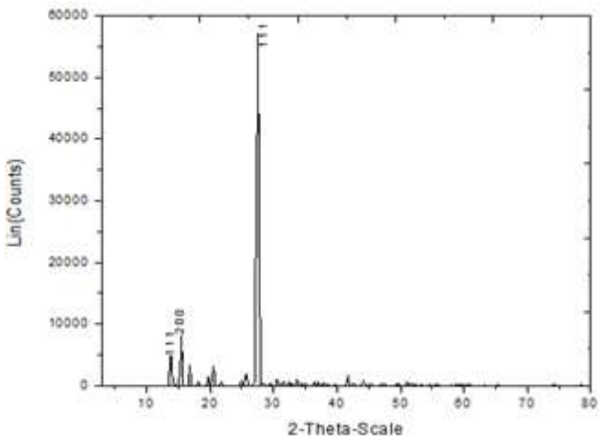

Fig.3.XRD pattern of Bisthiourea Zinc Chloride

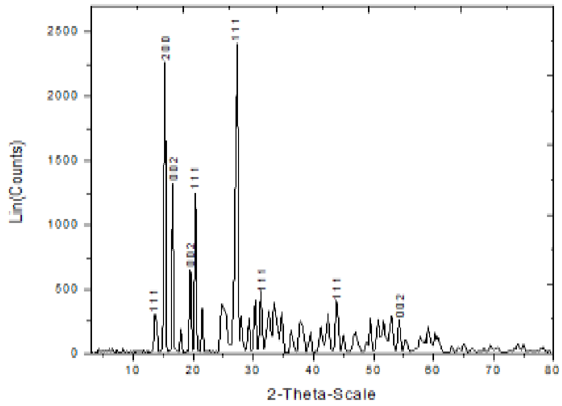

Fig.3.XRD Pattern of Ferrous Sulphate doped BTZC

3.2 Fourier transforms infrared spectroscopy (FTIR) analysis

In order to analyze the presence of ferrous sulphate in BTZC crystal qualitatively, Fourier transform infrared spectra carried out. FTIR spectrum was recorded in the wavelength range 500-4500cm-^{1}. The FTIR spectra of pure and ferrous sulphate doped BTZC crystal is shown in figure, Fig (5) shows the intensity 3285.58cm^{-1} is due to Asymmetric NH_2 stretching vibration. The peak observed at 3200.66cm^{-1} is assigned to symmetric NH_2 stretching vibration. The Asymmetric C=S stretching vibrations occurs at 1403.84cm^{-1}. The C=S stretching vibration is shifted to lower values from 727.83 to 712.35 cm^{-1} and this shifting of C=S stretching frequency confirms the coordination of metal-sulphur bond. The peaks at 1614.57cm^{-1} is due to NH_2 bending vibration. Symmetric N-C-N stretching vibration peak at 1099.41cm^{-1}. Asymmetric N-C-N stretching vibration peak at 1493.18cm^{-1} the symmetric C=S stretching vibrations occurs at 712.35cm^{-1}. The $FeSO_4$ doped BTZC absorption bands are compared to pure BTZC C=S Stretching decreases and N-C-N, stretching increases, this confirm the shift may be due to doping of Ferrous Sulphate.

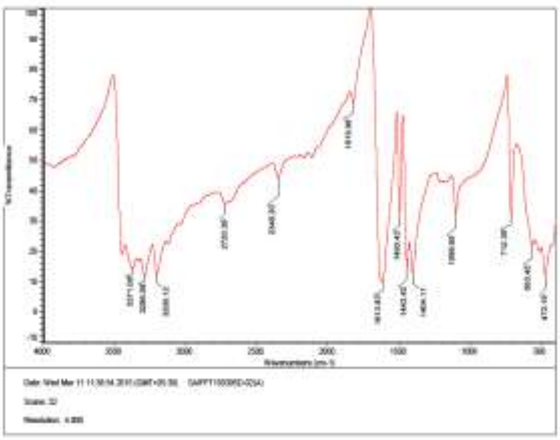

Fig.4. FTIR Spectrum of Bis thiourea Zinc Chloride

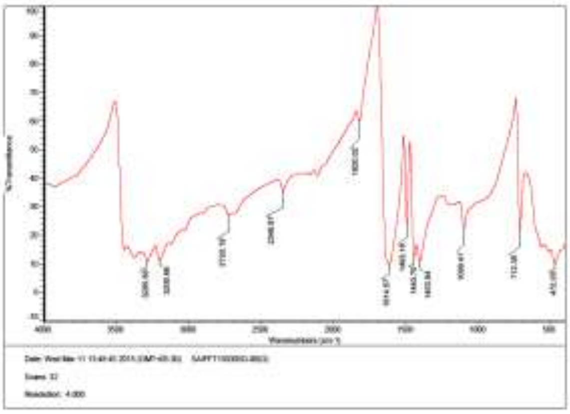

Fig.5. FTIR Spectrum of Ferrous sulphate doped BTZC

Table-3: **The Comparison and assignment of FTIR bands of pure and$FeSO_4$doped BTZC**

Assignment	Thiourea (LR)	Pure BZTC	$FeSO_4$ doped BTZC
AsymmetricN H_2Stretching	3276.85	3286.08	3285.58
Asymmetric NH_2 Stretching	3175.93	3200.12	3200.66
NH_2 Bending	1616.38	1613.83	1614.57
Asymmetric N-C-N Stretching	1468.32	1493.43	1493.18
Asymmetric C=S Stretching	1411.43	1404.11	1403.84
Symmetric N-C-N Stretching	1080.97	1099.65	1099.41
Symmetric C=S Stretching	727.83	712.39	712.35

3.3 UV-Visible spectral analysis

The single crystals are mainly used for optical application. Thus the study of optical transmission range of grown crystal is important. The optical transmission spectrum was recorded wavelength region 200-700nm. The transmittance spectra show the grown crystals have lower cutoff wavelength at around 232nm for BTZC crystal. The grown ferrous sulphate doped BTZC crystal has good transmission in UV as well as in visible regions. The forbidden band gap for the grown crystals of this work was calculated using the relation E=hc/λ, where 'h' is the plank's constant, 'c' is the velocity of light 'λ' is the cut-off wavelength. The grown crystal has good transmission in UV as well as in visible region. This is an added in the field of optoelectronic applications. The band gap and lower cut-off wavelength are shown in table.3. The lower cut of wavelength and low percentage of absorption indicates that the crystal readily allows the transmission of the laser beam in the range between the 300nm to 700nm, and application for high power frequency conversion. It shows that the grown crystal has a good transparency in UV-Visible and near IR region indicating that it can be used for NLO application(5). Ferrous sulphate doped BTZC lower cut off wavelength are greater than pure BTZC. This high value of 5.31312 eV band gap energies shows the crystal posses dielectric behaviour to induce polarization when powerful radiation is incident on the material. The large energy band gap also confirms that the defect concentration in the grown crystal is very low. The obtained value for the forbidden gap for all crystals was shown in table.

Table-3: Lower cut off wavelength and band gap energy of pure and Ferrous sulphate doped BTZC

Sample	Lower cut off Wavelength(nm)	Band gap energy(ev)
Pure BTZC	232	5.355
Ferrous sulphate doped BTZC	233.83	5.31312

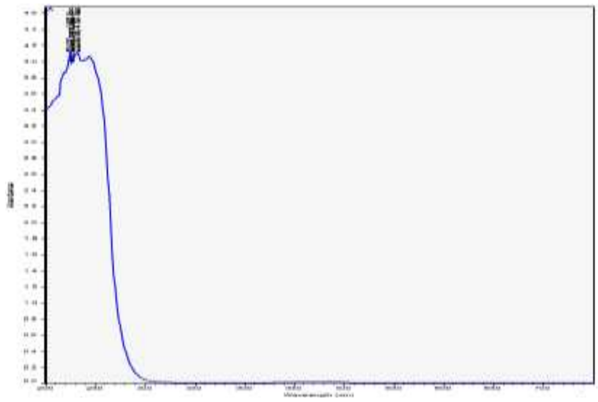

Fig.6. UV Spectrum of Bis thiourea Zinc Chloride

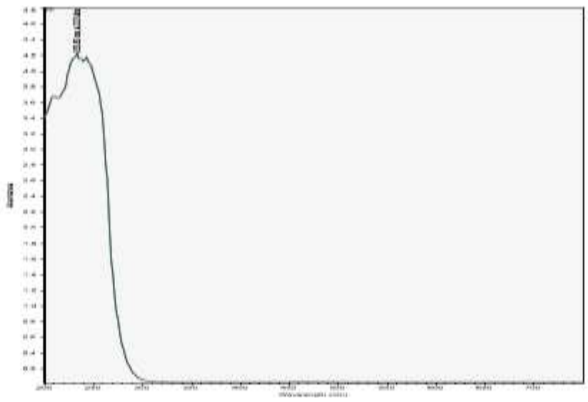

Fig.7. UV Spectrum of Ferrous Sulphate doped BTZC

3.4 Thermal analysis

Differential Thermogram analysis(DTA) and thermo gravimetric analysis(TGA) gives information regarding as the Phase transition temperature, melting point and the weight loss of the grown crystal, water of crystallization and different stages of decomposition of the pure and Ferrous sulphate doped BTZC crystal system were determined by thermo gravimetric(TGA) by using TAQ-500 analyzer. Thermal analyzer in the temperature range 40^{o}C to 730^{o}C. The TGA & DTA Spectrum of Ferrous sulphate doped BTZC. The TGA curve shows that the sample undergoes a complete decomposition between 230^{o}C to 730^{o}C, these curves shows that the loss of weight occurs in three steps. The first weight losses in 22.97% are due to liberation of volatile substance, sulphur oxide and second weight loss occurs due to organic compound evaporation in 75.82% and third weight loss occurs due to the residue at 79.26%. From DTA curves shows the endothermic peaks. The sharpness of the endothermic peak shows good degree of Crystallinity of the grown crystal. There is no weight loss up to 237.24^{o}C, which indicates the melting point of the crystal and absence of water in the grown crystal. The decrease in thermal stability due to the presence of ferrous sulphate doped BTZC is observed from thermo gravimetric analysis. This temperature range of the grown crystals ensures the possibility of the crystals for NLO application.

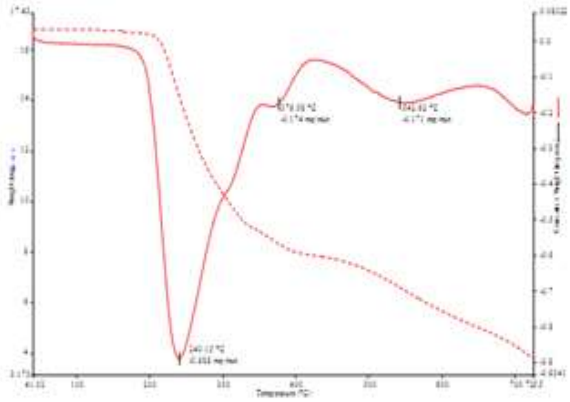

Fig.8. TGA&DTA Spectrum of Bis thiourea Zinc Chloride

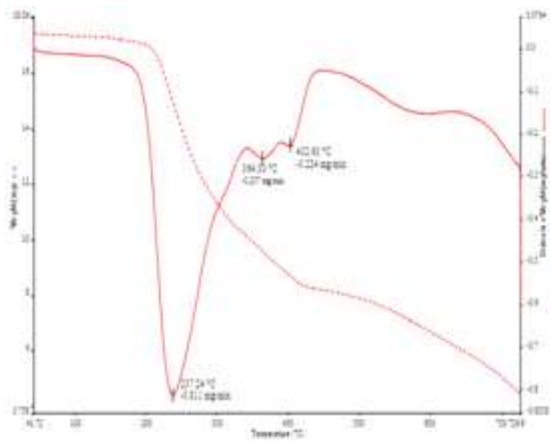

Fig.9. TGA&DTA Spectrum of Ferrous Sulphate doped BTZC

3.5 Energy Dispersive X- ray Analysis

The elemental compositions of the pure and ferrous sulphate doped Bis thiourea Zinc Chloride are carried out by EDAX spectroscopy. In order to confirm the presence of dopant in growing crystals. EDAX spectrum of pure and ferrous sulphate doped Bis thiourea Zinc Chloride is shown in Figure (10&11). The strong peaks observed in the spectrum are related to Nitrogen, Sulphur, Chloride, Zinc, iron. Ferrous sulphate doped BTZC were found to have atomic percentage at 31,60 of N, 27.50 of S, 27.93 of Cl,12.86 of Zn,0.12 of Fe . This confirms the doping of ferrous sulphate in the BTZC crystal.

Table-4: EDAX data of the pure and ferrous sulphate doped BTZC crystal

Crystal	Element	Weight %	Atomic %
Pure BTZC	N	26.21	50.27
	S	23.87	20.00
	Cl	26.54	20.11
	Zn	23.38	9.61
Ferrous sulphate doped BTZC	N	14.18	31.60
	S	27.89	27.50
	Cl	31.32	27.93
	Zn	1.49	12.86
	Fe	0.22	0.12

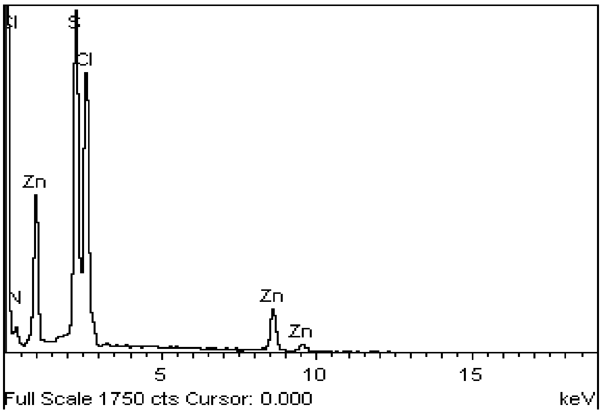

Fig.10. EDAX Spectrum of Bis thiourea Zinc Chloride

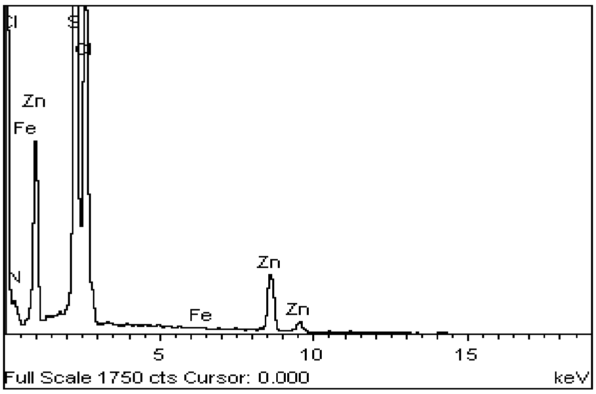

Fig.11.EDAX Spectrum of Ferrous Sulphate doped BTZC

IV. CONCLUTION

Single crystals of ferrous sulphate doped crystals were grown by the aqueous solution method with the slow evaporation technique at room temperature. Sharp peaks of powder XRD spectrum of the crystal show good crystalline nature of the compound. The presence of various functional groups was confirmed by FTIR analysis. EDAX spectrum confirms the presence of ferrous sulphate in BTZC crystal. UV-Visible study show that the grown crystal has wide range of transparency in UV and entire visible region and cutoff wavelength of ferrous sulphate doped BTZC is around 233.83nm.The decrease in thermal stability due to the presence of Ferrous sulphate doped BTZC is observed from thermo gravimetric analysis. The promising crystal growth characteristics and properties of pure and ferrous sulphate doped BTZC crystal makes it suitable for optical devices applications.

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