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Growth and characterization of Pure and L-alanine doped ZTC Crystals

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ABSTRACT

Single crystals of pure Zinc Tris-thiourea Chloride (ZTC) and L-alanine- doped ZTC were grown from aqueous solutions by slow evaporation technique. The grown crystals have been subjected to single crystal x-ray diffraction to determine the unit cell dimensions. The Fourier Transform Infrared (FT-IR) spectra has been recorded in the range 400-4500 cm^{-1}. Morphological alterations have been observed when L-alanine was doped into ZTC crystals. UV-Visible spectrum shows that the grown crystals have wide optical transparency in the entire visible region. The grown crystals were also subjected to other characterizations such as micro hardness, thermal and NLO studies.

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1. Introduction

Semiorganic Nonlinear optical materials posses wide range of applications in the field of telecommunication optical information storage devices. These materials have large nonlinearity, high resistance, too large induced damage, low angular sensitivity and good mechanical hardness [1-3]. Recently metal complexes of thiourea have been explored. Some of the potential thiourea complexes are zinc thiourea chloride (ZTC), zinc thiourea sulphate(ZTS), cadmium thiourea chloride (BTCC), copper thiourea chloride (CTC), bis thiourea zinc acetate (BTZA) and cadmium thiourea acetate (BTCA). These crystals have better nonlinear optical property than KDP [4-8].Growth of ZTC single crystals using slow evaporation technique at room temperature has already been reported [9]. Influence of pH of the pure ZTC crystals has also been reported [10]. Investigation of nucleation kinetics of pure ZTC and L-Arginine doped ZTC have been carried out and reported in the earlier studies [11, 12]. The centrosymmetric thiourea molecule , when combine with inorganic salt yield non symmetric complexes, which has the nonlinear optical properties [13]. A series of studies on semiorganic amino acid compounds such as L-arginine phosphate [14], L- histidine hydrobromide [15], L-cystine hydrochloride [16],L-valine hydrochloride[17] as potential NLO crystals have been reported. The NLO properties of some complexes of thiourea have attracted significant attention because both organic and inorganic components in it contribute specifically to the process of SHG [18-20] ZTC is a potential semiorganic nonlinear material and crystallizes in the noncentrosymmetric orthorhombic sapce group. Though the SHG efficiency of ZTC is reported to be less than that of ZTS [9], it has promising crystal growth characteristics.

In the present study, the characterization of pure ZTC crystals and the effect of amino acid L-alanine as an added additive (1mol %) on characterization of these crystals are investigated. It has been observed that the additive has control on the crystallization which is conformed by comparing the results of pure and amino acid doped ZTC single crystals.

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2. Experimental

2.1. Crystal growth

The material of the title compound was synthesized in the aqueous medium from zinc chloride and Thiourea in 1:3 stoichiometric ratio according to the following chemical reaction.To avoid decomposition, low temperature(room temperature) was maintained during preparation of the solution in the deionized water.

The solution was stirred with magnetic stirrer and the mixture was heated at 50 °C till a white crystalline salt of ZTC was obtained.

$$ZnCl_2+2[CS(NH_2)_2]\text{--}\rightarrow Zn[CS(NH_2)_2]_2Cl_2$$

Single crystals of ZTC and L-alanine doped ZTC were grown employing slow evaporation techniques. Transparent colorless ZTC crystals of size 15 x 12 x 2 mm^3 were harvested in 30 days. For the growth of L-alanine doped ZTC crystals, 1 mol percent of L-alanine was added to the solution of ZTC. Single crystals of size 10 x 9 x 2 mm^3 with good transparency were harvested in 30 days as shown in Fig (1a) and (1b).The molecular structure is shown in Fig(2).

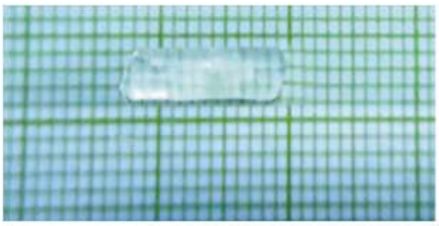


Fig (1a). The Photograph of Pure ZTC

Fig (1b).The Photograph of L-Alanine Doped ZTC Crystal

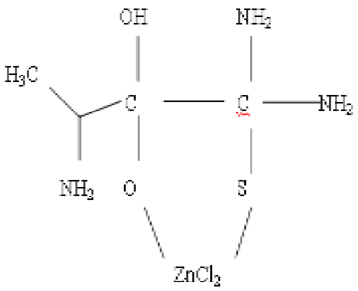


Fig (2). Molecular structure of ZTC crystal

3. Characterization

The structural and optical behavior of the grown crystals were examined by single crystal and powder X-ray diffraction, FTIR, and UV-Vis NMR studies respectively. The mechanical and thermal properties of the grown sample were analyzed by Vicker's micro hardness and thermal studies. The SHG conversion efficiency of the sample was also measured.

3.1. X-ray diffraction analysis

The single X-ray diffraction studies have been carried out to confirm the crystallinity and to determine the lattice parameters of the grown sample. The single crystal X-ray diffraction has been carried out using ENRAF NONIUS CAD4 diffractometer. The structure was solved by the direct method using SHELXL program. From the XRD data it is observed that both pure and L-alanine doped ZTC crystals are orthorhombic. The calculated lattice parameter values of pure and L-alanine doped ZTC are presented in table (1). The results of the present work are in good agreement with the reported values [21]. In the case of doped sample, a slight variation in the cell volume is observed.

This has been confirmed by powder XRD diffraction analysis by using a Rich Seifert diffractometer with $C_uK_\alpha(\lambda=1.5417A°)$ radiation. The powder XRD pattern of pure and L-alanine doped ZTC crystals are shown in fig (3a) and (3b). The orthorhombic structure of the grown crystals have been confirmed and Table. (2a) and (2b) gives the d spacing & their respective indices. The well-defined peaks at specific 2θ values show high crystallinity of the grown crystals. This work was indexed using the TREOR software package following the procedure of Lipson and Steeple [22]. Also UNIT CELL software package was used to confirm the indexing.

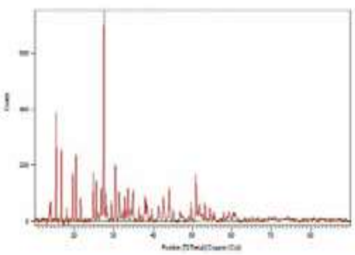


Fig (3a).Powder XRD patterns of ZTC crystal

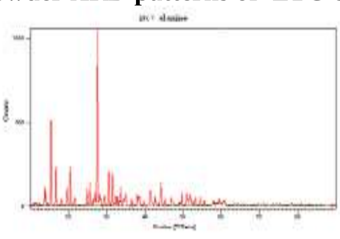


Fig (3b).Powder XRD Patterns of L-Alanine Doped ZTC Crystal

3.2. FTIR

The infrared spectroscopy is effectively used to identify the functional groups of the samples. FT-IR spectra of pure and L-alanine doped ZTC crystal were recorded in the KBr pellet technique in the frequency region 400-4000 cm^{-1} using PERKIN ELMER RX1 Fourier Transform Infrared spectrometer and the spectra are shown in Fig.(4a) and (4b).The frequencies and the corresponding assignments are given in Table.(3).

In the FTIR spectrum of ZTC , the intensity 3368 cm^{-1} is due to N-H stretching vibration of the NH_2 group of thiourea. The C=S stretching vibrations occurs at 1622 cm^{-1}. The peaks at 1494 and 1401 cm^{-1} are due to HN_2 bending vibration. C-N vibration is a peak at 1098 cm^{-1} .

The peaks at 711 and 473 cm^{-1} are tentatively assigned to Zn-S vibrations. So the crystal is devoid of covalent bonded water to Zinc. The spectrum of L-alanine doped ZTC displays nearly similar features as that of ZTC, hence this crystal is also not having water in its lattice. Examinations of the peak position illustrates substantial shifts for the peaks at 3368, 1622,1494,1401,1098,711 and 473 cm^{-1}. This is the clear indication for the presence of amino acid, L-alanine in the lattice of ZTC crystal.

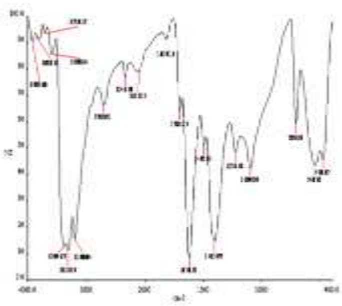


Fig (4a). FTIR Spectrum of ZTC crystals

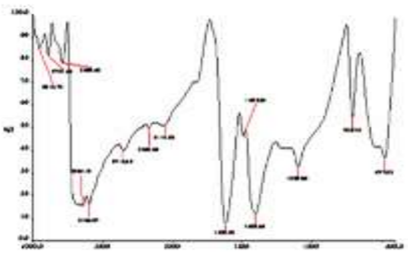


Fig (4b). FTIR Spectrum of L-Alanine Doped ZTC Crystals

3.3. UV-Visible transmittance study

The UV-Vis-NMR transmission spectrum of pure and L-Alanine doped ZTC single crystals were recorded in the range of 200-1100 nm and is shown in the fig (5a) and (5b).

The instrument used was LAMBDA-35 UV-Vis spectrophotometer. From the spectrum, it is seen that the lower cut off wavelength of both pure and L-alanine doped ZTC crystals are around 300 nm. The spectrum further indicates that the crystal has wide optical window from 300 nm to 1100 nm.

It is observed that through the transparency of the grown ZTC crystals is more than L-alanine doped ZTC crystal, there is no change in the optical window. The transparency in the entire visible region shows that this material is a best suitable candidate for opto electronic application.

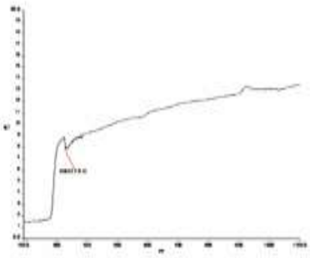


Fig (5a) UV-Vis spectrum of ZTC crystal

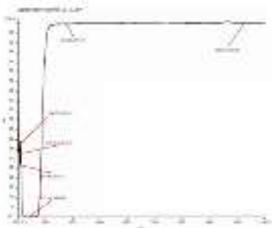
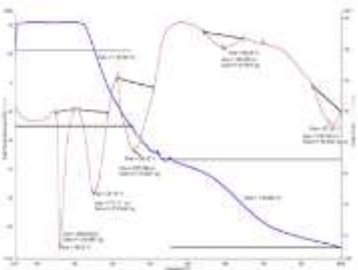


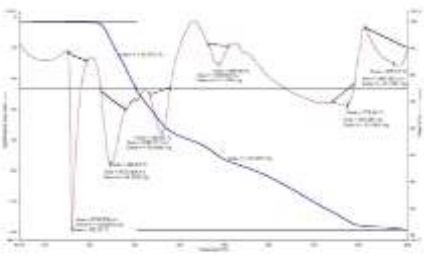
Fig (5b) UV-Vis spectrum of L-alanine doped ZTC crystal

3.4. Thermal Analysis

The thermal analysis (TGA) was carried out by using TAQ-500 analysier at a heating rate of 25^0 C/ min for temperature range 50 to 900^o in nitrogen inert atmosphere to study the weight loss and thermal stability. The thermogram is shown in fig (6a) and (6b). It reveals that the major weight loss of about 48% takes place in the region 238.75^o C and 293.28^o C. The crystals are stable upto the temperature of 238.75^o. There is no weight loss upto 100^o C, ensuring the absence of water in the crystal structure. The first weight loss is due to decomposition of both the compounds and the second weight loss of about 52% is due to organic compound evaporation and liberation of volatile substances like sulphar dioxide. The sharpness of the endothermic peak shows good degree of crystallinity of the grown crystal. In the DTA curve the first endothermic peak has been observed at 238.75^oC for L-alanine doped ZTC crystal which is nearly 40^oC higher than pure ZTC crystal. Hence it is confirmed that the melting point of L-alanine doped ZTC crystal which is 238.75^oC is higher than pure ZTC crystal. Thus the grown crystal is a best suitable material for NLO application.



Fig(6a). TG and DTA Thermograms of ZTC Crystals



Fig(6b). TG and DTA Thermograms of L-Alanine Doped ZTC Crystals

3.5. Vickers hardness test

Vickers microhardness indentation test is used to characterize the hardness of the material. The hardness number can be evaluated by the knowledge of the load applied and the cross-sectional area of the depth of the impression. Smooth surfaces of as-grown L-alanine doped ZTC crystals were chosen for the investigation. The Vicker's 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 indented impressions.

In the present study, hardness was measured using Leitz-Wetzler hardness tester. Different loads were applied at a time of 10 seconds. The indentation marks were obtained and measured in terms of the diagonal length (d). Six trails were performed at each load to minimize the error.

Plot of load (P) against Vicker's hardness (H_v) is shown in the figure (7a) and (7b). It is observed that the microhardness increases with the increase of load at lower values which can be attributed to the work hardening of the surface layers.

At higher loads beyond 75gms the microhardness shows a tendency to saturate. Significant cracking occurs which may be due to the release of internal stresses generated locally by indentation [23]. The relation connecting the applied load(P) and diagonal length (d) of the indenter is given by the Meyer Law[24]. From Meyer's Law $P=ad^n$ connecting the applied load (P) and diagonal length (d) of the indentation, the work hardening coefficient 'n' was calculated. Here 'a' is a constant for a given material From the observations on various materials [25,26] it is pointed out that 'n' lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials. Here for both pure and L-alanine doped ZTC single crystals, the calculated value of 'n' is greater than 1.6 whicht suggests that the grown crystals are relatively soft.

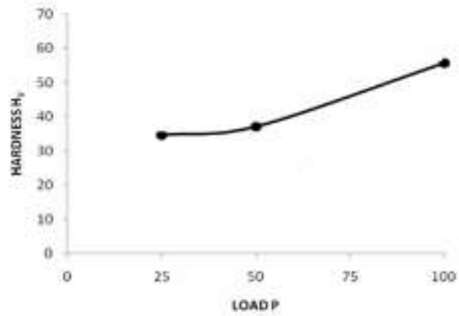


Fig (7a).Vickers Hardness Vs load for ZTC Crystals

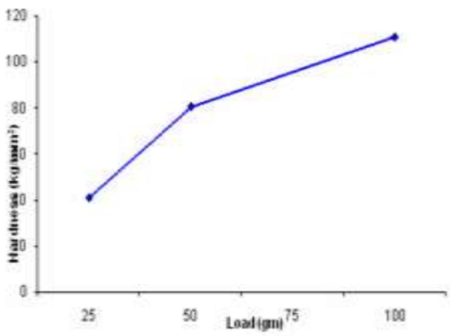


Fig (7b).Vickers Hardness Vs load for L-Alanine Doped ZTC Crystals

3.6. SHG efficiency measurement

The grown crystals were subjected to the NLO study to measure the efficiency with respect to pure ZTC. The SHG property of a grown crystal was tested by the Kurtz and Perry powder method [27].The fundamental beam of wavelength 1064 nm from a Q-switched Nd:YAG laser with a pulse energy 3mJ/pulse, pulse width 8ns,and repetition rate 10 Hz was used.

The salt of 1 mole % L-alanine doped ZTC was packed in a micro capillary of uniform bore and exposed to laser radiations. The SHG conversion efficiency of L-alanine –doped ZTC was found to be enhanced than that of pure ZTC. The optical signal generated from the sample was converted into an electrical signal and was measured using an oscilloscope.The measured outputs for pure ZTC and 1mole% L-alanine doped ZTC were 5mV,12mV respectively.This indicates that the SHG conversion efficiency of 1mole % L-alanine-doped ZTC is greater than pure ZTC. SHG efficiency is 2.8 times than that of pure ZTC crystals.

4. Conclusion

Good optical quality pure ZTC and L- alanine doped ZTC single crystals have been grown by solution growth method at room temperature. The lattice parameters have been found by single crystal X-ray diffraction technique. The FT-IR spectrum reveals the presence of various functional groups in the grown crystal. The optical absorption spectrum reveals that the absorbance is less between 300 and 1200 nm. This illustrates the absence of any overtones or combination modes above 250 nm and absorbance due to electronic transition between 300 and 1100 nm. The Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. Hardness measurement also shows that L-alanine doped crystals are much harder than pure ZTC crystals and like pure ZTC single crystals , the L-alanine doped ZTC single crystals are also of soft nature. The TG/DTA curve of this sample indicates that the sample is stable up to 238.75^0c. The sharpness of the endothermic peak shows good degree of crystallinity of the grown crystal. Second harmonic generation was observed using a Q-swiched nd:YAG laser and the SHG efficiency was found to be 2.8 times higher than pure ZTC. Thus promising crystal growth characteristsics and good optical properties with the moderate SHG efficiency make L-alanine doped ZTC single crystal a potential material for photonic device applications.

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Table. 1 Single Crystal XRD data of pure and L-alanine doped ZTC crystals.

ZTC (Reported)	L-alaninedoped ZTC
a = 13.014 A°	a = 13.017A°
b = 12.772A°	b = 12.764 A°
c = 5.893 A°	c = 5.898 A°
V= 978.59 $A^{\circ 3}$	V = 980.94 $A^{\circ 3}$
Orthorhombic	Orthorhombic
Pnma	Pnma

Table (2a). X-ray powder diffraction data of ZTC crystals

2θ	d-spacing [Å]	FWHM
14.0112	6.32090	0.1338
15.3908	5.75729	0.2342
16.7261	5.30054	0.2007
18.0195	4.92290	0.4015
19.5758	4.53488	0.1673
20.3677	4.36033	0.2007
21.5879	4.11654	0.1338
24.8022	3.58986	0.1673
25.5474	3.48681	0.2007
26.8417	3.32155	0.1338
27.4720	3.24676	0.2007
28.0860	3.17716	0.1338
29.3977	3.03832	0.1338
30.4017	2.94022	0.1840
31.3074	2.85720	0.2509
32.7340	2.73587	0.2007
33.5980	2.66746	0.1673
34.9125	2.56998	0.3011
36.3750	2.46994	0.1673
38.3204	2.34891	0.3346
39.6370	2.27387	0.2676
41.4291	2.17956	0.5353
42.5985	2.12239	0.4684
44.0934	2.05385	0.2007
46.8068	1.94092	0.3346
49.6043	1.83781	0.1673
50.9094	1.79372	0.2676
53.1868	1.72216	0.2676
54.4541	1.68504	0.2676
57.9158	1.59230	0.2676
60.8612	1.52084	0.8160

Table (2b).X-ray powder diffraction data of L-alanine doped ZTC crystals

θ	d-spacing [Å]	FWHM
13.7701	6.43101	0.2007
15.4609	5.73133	0.2007
16.7714	5.28631	0.2007
19.6337	4.52164	0.2007
20.5127	4.32982	0.2342
21.6777	4.09969	0.2676
24.8257	3.58651	0.2342
25.6351	3.47509	0.2175
26.9054	3.31383	0.2007
27.4847	3.24528	0.2676
29.4584	3.03219	0.2676
30.5300	2.92816	0.1673
31.4777	2.84213	0.1673
32.7654	2.73332	0.2342
33.6421	2.66407	0.2007
34.9594	2.56665	0.2676
36.4121	2.46751	0.2676
36.9645	2.43189	0.2676
37.9369	2.37177	0.2007
38.5419	2.33592	0.3346
39.6814	2.27143	0.2676
41.3302	2.18455	0.2007
42.6328	2.12077	0.3346
44.1453	2.05155	0.2007
45.2195	2.00529	0.2676
46.9760	1.93432	0.6691
49.7251	1.83363	0.2676
50.9988	1.79079	0.2676
51.9922	1.75888	0.5353
53.2289	1.72090	0.3346
54.5186	1.68320	0.3346
55.6563	1.65146	0.5353
60.7356	1.52369	0.6528

Table (3) FTIR data comparison of thiourea with pure and L-alanine doped ZTC crystals

ZTC(Measured)	L-alanine doped ZTC	ASSIGNMENT
3368	3086	N-H stretching
1622	1616	C=S stretching
1494	1456	NH_2 bending
1401	1412	NH_2 bending
1098	1109.58	C-N vibration
711	772.05	Zn-S vibrations
473	411.64	Zn-S vibrations