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Studies On Growth Structural, Electrical, Mechanical And Optical Properties Of Pure And Doped Bis Thiourea Cadmium Acetate (BTCA)

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ABSTRACT
Metal organic coordination complex single crystals bis thiourea cadmium acetate (BTCA) and L cystein doped BTCA have been synthesized and grown successfully by slow evaporation technique using water as solvent at room temperature. The lattice parameters were analyzed by single crystal X-ray diffraction technique. The surface analysis of the grown crystal was studied using AFM studies and the results are discussed in detail. The optical properties of these crystals were investigated by UV–Visible as well as photoluminescence spectroscopy. The mechanical stability of the grown crystals was confirmed through Vickers micro hardness study. By parallel plate capacitor technique, the dielectric response was studied over a wide range of frequencies.
Keywords - Thiourea, AFM, solution growth, non linear optical crystal, Microhardness

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I. INTRODUCTION

Nonlinear thiourea metal complexes with high mechanical hardness, structural stability, high optical and nonlinear behavior are advantageous for applications in the fields of optical information-storing devices, second harmonic generation (SHG), nonlinear optical (NLO) and telecommunication systems [1].Thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [2]. The centrosymmetric thiourea molecule, when combined with inorganic salt yield noncentrosymmetric complexes, which has the nonlinear optical properties [3]. A large family of thiourea metal complexes include zinc thiourea sulphate (ZTS), zinc thiourea chloride (ZTC), copper thiourea chloride (CTC), bis thiourea zinc acetate (BTZA), bis-thiourea cadmium acetate (BTCA), bis thiourea cadmium formate (BTCF), potassium thiourea chloride (PTC), potassium thiourea bromide (PTB) and potassium thiourea iodide (PTI) has been reported in literature[3-10] .]. L-Cystein the smallest naturally occurring aminoacid with a thiol group offers a high degree of chirality due to the presence of three different functional groups[10].It has Zwitter ionic state in aqueous solution as well as in solid state[11].

The present work deals with growth of pure and L-cystein doped BTCA single crystals and determination of its Structural ,optical ,mechanical and electrical properties.

II. EXPERIMENTAL DETAILS

BTCA salt was synthesized by dissolving cadmium acetate and thiourea in deionized water in the molar ratio 1:2 according to the reaction:

$$2[CS(NH2)2] + Cd(C2H3O2)2 \rightarrow Cd[CS(NH2)2]2\ (C2H3O2)2$$

The supersaturated solution of the synthesized salt was stirred well for 6 hours to yield a homogenious solution using magnetic stirrer. The solution was filtered using whatman filter paper and kept for evaporation at room temperature. The purity of the synthesized salt was improved by successive recrystallisation process.

The same procedure was applied to grow L-cystein doped crystals by adding 2 wt% concentration of L-cystein to the mother solution . Single crystals of pure and L-cystein doped BTCA were harvested in a period of 20-25 days.The grown crystals are shown in figure. 1

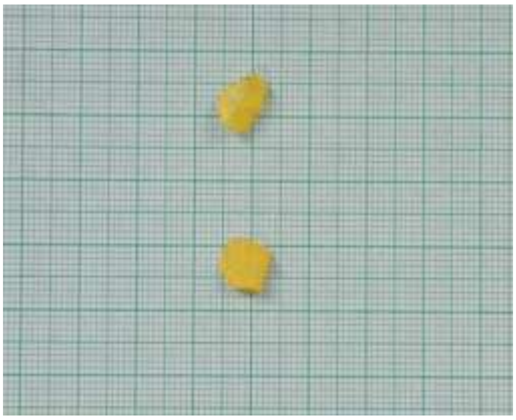

Fig 1: Photograph of L- BTCA single crystal

III. RESULTS AND DISCUSSION

3.1 Single crystal 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.[8]
The cell parameters of L-Cystein doped BTCA crystal was carried out by single crystal XRD technique using Bruker Kappa Apex II diffractometer.The determined lattice parameters of L-Cystein doped BTCA crystal are tabulated in table 1 and compared with pure BTCA reported[18]. The doped BTCA crystals are belong to the orthorhombic system and there are variations in lattice parameters when compared with pure. The change in lattice parameters confirms the presence of L-Cystein in BTCA crystal. The PLATON diagram of L-Cystein doped BTCA is also shown in figure 2.

Chemical formula	BTCA (reported[18])	L-cystein doped BTCA
Cell Parameters	a = 7.5758 A˚ b = 15.4327 A˚ c = 11.8230 A˚	a = 7.5780(6) A˚ b= 15.4280(10) A˚ c= 11.7997(9) A˚
Volume	1382.27 A^3	1379.54(18) A^3
System	Orthorhombic	Orthorhombic
Space group	P21/n	P21/n

Table 1: Single crystal data of undoped and L-cystein doped BTCA

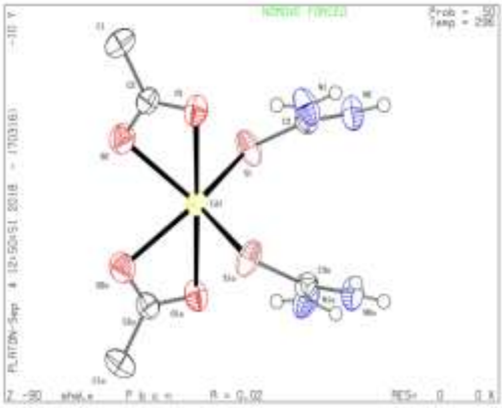

Fig 2: The PLATON diagram of L-Cystein doped BTCA

3.2 AFM Analysis

The surface analysis of the as pure and doped grown crystal was done by atomic force microscopy in semi contact mode. Figure 3 and figure 4 shows the AFM images of Pure and doped BTCA crystal. The images reveal that the surface of pure and doped BTCA contains number of peaks and valleys. The surface roughness parameters are shown in Table 2 which indicates that the crystal possesses almost smooth surface. For pure and doped BTCA crystal the surface skewness (Ssk) value is very low (0.12 & 0.11) which confirms that the surface has more valleys than peaks and hence the surface is planar (Rajesh kumar et al 2010). Ssk also indicates the load carrying capacity and porosity of the material and the low skewness is a criterion for a good bea ring surface (Rajesh Kumar and Subba Rao 2012).The ten-point height of the surface (Sz) is found to be 0.22 and 0.32 nm. Surface kurtosis (Sku) is the measure of surface sharpness and for pure and doped BTCA crystal the Sku is less than three which indicates that the surface is perfectly flat. From the study, it reveals the pure and doped BTCA crystal has smooth and flat surface.

S.NO	AMPLITUDE PARAMETER	BTCA PURE	BTCA DOPED
1	Roughness average (Sa)	19.29 nm	21.33nm
2	Root mean square (Sq)	29.17nm	19.21nm
3	Surface skewness (Ssk)	0.12	0.11
4	Surface kurtosis (Sku)	0.38	0.46
5	Ten-point height (Sz)	0.22	0.32

Table 2: Surface parameters of Pure and doped BTCA measured by AFM

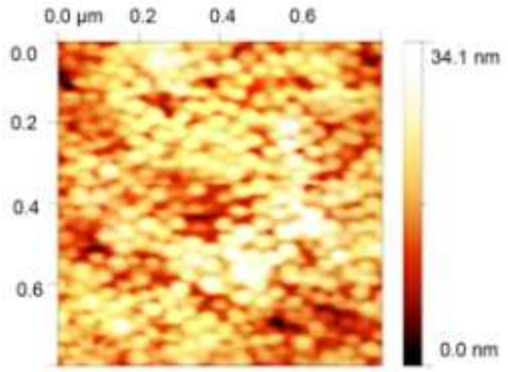

Fig 3: AFM image of Pure BTCA

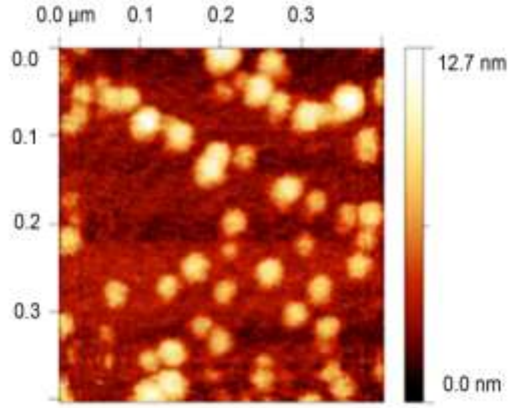

Fig 4: AFM image of doped BTCA

3.3 UV –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 optical absorbance and transmittance spectra of pure and doped crystals are shown in the figure 5 and figure 6.From the transmission spectrum it is observed that both the crystals showed very high transmission at entire IR and visible region.The transmission for L-Cystein doped BTCA crystal is found to be higher than that for pure BTCA. The transmittance in the entire visible region suggest these crystals are suitable for second harmonic generation devices [20].

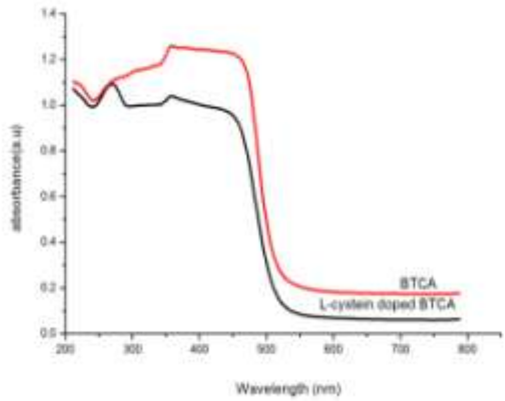

Fig 5: Optical Absorbance Spectra of Pure and doped BTCA

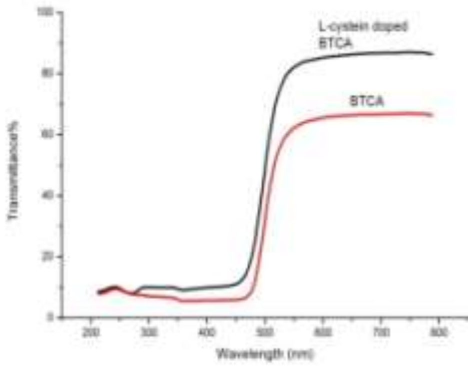

Fig 6: Optical transmittance Spectra of Pure and doped BTCA

3.4 Photoluminescence

The photoluminescence (PL) spectrum of both pure and doped BTCA were recorded by fluorescence spectrometer are shown in figure 7. single peak was observed at 400 nm in the spectrum of pure BTCA. The single broad emission confirms the structural perfection of the grown crystal. ln the spectrum of L-cystein doped BTCA two major peaks were observed at 406 nm and 434 nm.The sharp PL intensity confirms low transitional band gaps and high optical quality of doped crystal substantiating it for NLO applications[19].

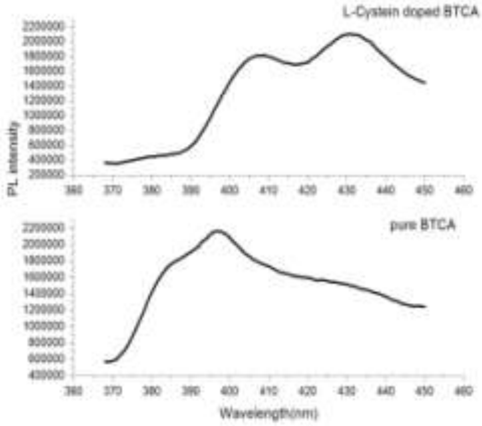

Fig 7: Photoluminescence spectrum of pure and L-Cystein doped BTCA

3.5 Microhardness Measurement

Vickers microhardness indentation test is used to characterize the hardness of the material.The hardness number was calculated using Hv = 1.8544 xP/d^2 Kg/mm^2. Where Hv is the Vickers microhardness number, P is the applied load in Kg, d is the mean diagonal length of the indentation impression in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid.The figure 8, shows a graph between hardness number and applied load. The hardness number of both pure and doped B CA crystals were increase with increase in load. At higher loads above 100 g significant cracking occurs which may be due to the release of internal stress generated locally by indentation .Higher the hardness value ,greater was the stress required to form dislocation, thus confirming greater crystalline perfection[15]. Compared to parent material ,the dopant material has a higher hardness value . Hence the dopant increases the mechanical strength of the parent material.

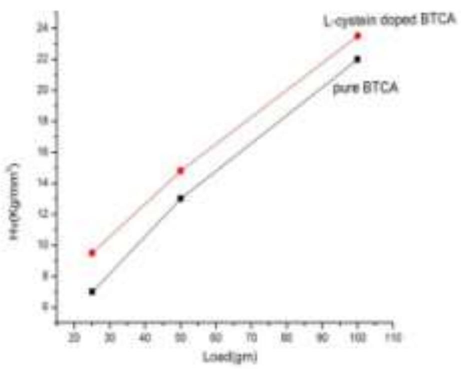

Fig 8: Hardness Vs load graph of pure and doped BTCA

3.6 Dielectric properties

The dielectric behavior of doped and pure BTZA crystal were carried out at room temperature using Agilent 4294A impedence analyser with varying frequency range of 40Hz to 110 MHz. The dielectric constant (εr) of both pure and doped BTCA were calculated using the equation, εr = Ct / εo A, where C is the capacitance, d is the thickness of the crystal, εo is the vacuum dielectric constant and A is the area of the crystal.

The variation of dielectric constant of pure and doped BTCA as a function of frequency is shown in Figure 9. The values of dielectric constant decrease with increase in frequency. At a fixed frequency, the dielectric constant of L-Cystein doped BTCA is more than that of pure one, which may be attributed to the higher polarizability of doped crystals [13,14]. The dielectric loss of pure and doped BTCA as a function of frequency is shown in fig. The values of dielectric loss also decrease with increase in frequency and it has low value in the higher frequency region. The low values of dielectric loss suggest that the grown crystals have lesser defects [4].The doped crystal shows increased dielectric loss compared to the pure one due to the occupation of dopant molecule in the crystal lattice which influences the polarization mechanism.

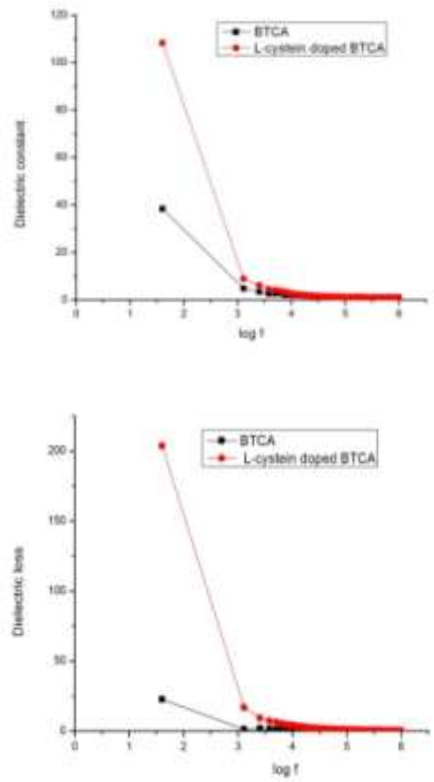

Fig 9: Variation of dielectric constant and dielectric loss with frequency of pure and doped BTZA

IV. CONCLUSION

Good quality single crystal of pure and L-cystein doped BTCA was grown by slow evaporation technique under room temperature. Grown crystals were characterized and compared with pure BTCA. Evaluation of lattice parameters confirms the dopents in to the lattice of the undoped BTCA crystal using single crystal XRD. The surface properties of the crystals were investigated Bt AFM and the results are discussed. Comparison study of Optical transmission confirms the improved quality of the doped crystals for NLO application. The photoluminescence studies of the doped sample confirms the quality of the crystals for photonic device applications. The mechanical property of both crystals were evaluated by Vickers micro hardness test and it is concluded that doped crystal is harder than pure one. Dielectric studies ascertained that the grown crystals possess low values of dielectric constant and dielectric loss with high frequency which is highly demanded for NLO applications.

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