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Thermal, hardness and nonlinear optical studies on pure and amino acids (L-Glutamic acid, L-Valine) doped Copper Thiourea complex crystals for Laser applications

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Amino acids (L-Glutamic acid, L-Valine) doped Copper Thiourea Complex crystals(CTC) are grown by solution growth technique. Slow cooling as well as slow evaporation methods were employed to grow these crystals. The concentration of dopants in the mother solution was 0.1 mol%. The solubility data for all dopants concentration were determined. There is variation in pH value and hence, there is habit modification of the grown crystals were characterized with FT-IR studies, SHG trace elements and dielectric studies reveal slight distortion of lattice parameter for the heavily doped CTC crystals. Thermal properties of the grown sample were analyzed by TG and DTA analysis. Mechanical properties of the amino acids doped CTC crystal were investigated by micro hardness studies. Moreover, the grown crystal shows high transparency in the visible and near IR regions. FT-IR spectra reveal strong absorption band at 1697 cm^{-1} for metal ion doped crystals. TGA–DTA studies reveal good thermal stability. The dopants increase the hardness value of the material and it also depends on the concentration of the dopants. Amino acids doping improved the NLO properties. The material shows relatively high SHG efficiency than that of KDP. The detailed results on the spectral parameters, habit modifications and constant values will be presented.

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Keywords: Solution growth, Solubility, Dielectric Studies, NLO properties

1. Introduction

In recent years several studies dealing with organic, inorganic and semiorganic molecules and materials called nonlinear optics (NLO) are being reported, due to the increasing need for cheap and easily processable materials for photonics applications. The nonlinear (NLO) responses induced in various molecules in solution and solids are of great interest in many fields of research [1, 2]. Thiourea molecules are an interesting inorganic matrix modifier due to its large dipole moment and its ability to form and extensive network of hydrogen bonds [3].The nonlinear optical properties of some of the complexes of thiourea, such as bis (thiourea) cadmium chloride (BTCC), bis (thiourea) zinc chloride (BTZC), tris (thiourea) zinc sulphate (ZTS), tris (thiourea) cadmium sulphate (CTS), potassium thiourea bromide (PTB) have gained significant attention in the last few years [4, 5 & 6], because both organic and inorganic components in it contribute specifically to the process of second harmonic generation. The centrosymmetric thiourea molecule, when combine with inorganic salt yield noncentrosymmetric complexes, which has the nonlinear optical properties [7]. Hence, in several years, search is focused on new types NLO materials which combined the advantages of organic and inorganic material called semiorganic materials. Two types of semiorganic material include organic and inorganic salts and metal organic coordination complexes [8, 9, 10, 12, 13 & 13]. Copper Thiourea Complex (CTC) is a good nonlinear optical semi organic material for second harmonic generation. CTC has high laser damage threshold, low angular sensitivity and wide range of transparency.

2. Experimental method

2.1 Selection of the Solvent

The Copper Thiourea Complex (CTC) material was purchased from Aldrich and it was purified by recrystallization process using water as a solvent. Organic crystal growth from solution mainly depends on the selection of a suitable solvent. Two major properties that would influence the crystal habit are assumed to be the difference in both the energy of crystallization and in the dipole moments between the crystallizing component and the solvent. If a solvent, which has similar dipole moment and the ideal solubility, is selected, large-size crystals can be expected to grow in the solution. On the other hand, a solvent has large differences in dipole moments from crystallizing substance and has poor solubility seems to be a poor solvent for the purpose of crystal growth with clear morphology. Most of the organic solvents have a dipole moment less than about 3Debye. Unfortunately, organic dielectric materials are usually highly polar in nature so that the selection of solvent is restricted. The choice of solvent with a large dipole moment is likely to produce a crystal with a better habit growth.

2.2 Crystal growth

A supersaturated solution of CTC powder is prepared in distilled, deionized water. The amount of CTC salt to be dissolved is determined from its solubility are at an average temperature of 35°C. The solution is stirred long enough to ensure complete dissolution of the solute, and filtered using Whatmann 100 filter paper to remove residual microscope particles. The solution is maintained [14, 15] at relatively high temperature for about 4–5 h using water circulation from temperature control unit. Pure CTC crystals were grown from aqueous solution by slow evaporation and also by slow cooling method. The same method was followed for doped CTC crystals (0.1 mol% L-Glutamic acid or L-Valine). The solubility (Fig.1) of doped CTC in the solvent was determined for each dopants for four different temperatures 30, 35, 40 and 45°C by dissolving the CTC salt in deionised water in an air-tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analysed gravimetrically. The solubility of doped CTC was measured for each dopant and was found to be 32.5-g/100 ml at 40°C for L-glutamic acid and 32.75-g/100 ml at 40^0C for L-Valine. The seed crystals are prepared at low temperature by spontaneous nucleation. Seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystal CTC and doped CTC (L-glutamic acid, L-Valine) were grown [figures.2(a), 2(b)] using a constant temperature bath (CTB), controlled with the Indtherm temperature programmer/controller . The mother solution was saturated using the initial pH values, 4.6 and 4.8 for L-Glutamic acid and L-Valine dopants respectively. The growth was carried out for more than 20 days by keeping the bath at a temperature of 38°C.

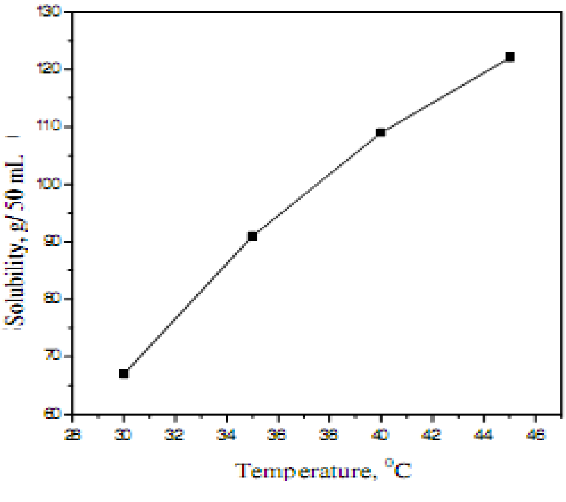

Fig. 1. Solubility curve solubility curve for CTCCrystal.

Fig..2(a)L-Glutamic acid doped CTC Crystal

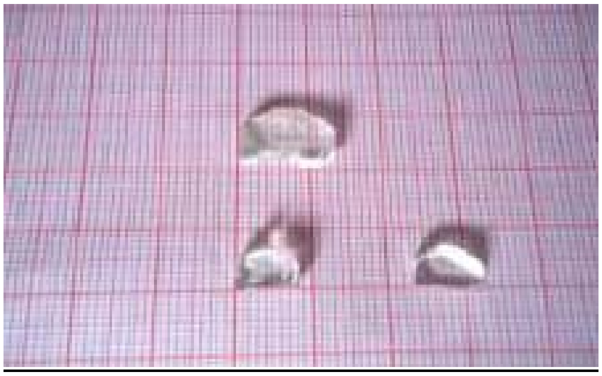

Fig. 2(b). L-Valine doped CTC Crystal

3. Powder X-ray diffraction analysis

Powder X-ray diffraction studies were carried out for the as grown crystals using a Rich Seifert X-ray diffractometer with CuK_α ($\lambda = 1.5405$ Å) radiation (Kurtz 1968). Powder X-ray diffraction spectra of the grown crystals fromL-Valine and L-Glutamic acid doped Copper Thiourea Complex are shown in Figures3,4.

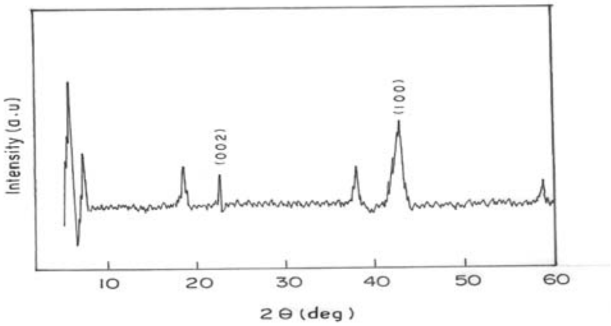

Fig. 3. XRD for L-Valine doped CTC

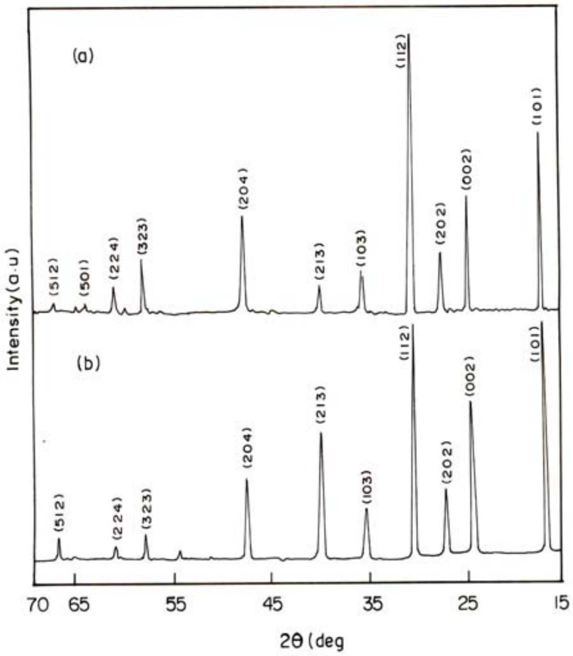

Fig. 4. XRD Spectra of (a) Cu-thiourea complex and (b) Cu-thiourea complex doped L-Glutamic acid.

Powder XRD spectra for the pure and Cu-Thiourea complex doped L-Glutamic acid revealed that the structures of the doped crystals were slightly distorted compared to the pure CTC crystal. This may be attributed to strain on the lattice by the absorption or substitution of Cu-thiourea complex. It is observed that the reflection lines of the doped CTC crystal correlate well with those observed in the individual parent compound with a slight shift in the Bragg angle.

4. FTIR studies

The FT-IR spectra of pure and amino acids doped Cu-thiourea complex crystals on a Bruker IFS 66V model spectrophotometer using 1064 nm output of a cw diode pumped Nd: YAG laser as a source of excitation in the region 500 – 4000 cm^{-1} operating at 200 mW power at the samples with a spectral resolution of 2 cm^{-1}. The observed FT-IR spectra of pure and doped CTC are shown in Fig.5. N-H is one of the prominent functional groups of the primary aromatic amines, and its asymmetric stretching vibration is observed at 3369 cm^{-1} and the symmetric stretching vibration is observed at 3286 cm^{-1}. The aromatic C–H stretching is observed at 3088 cm^{-1} and the aliphatic C-H stretching is observed at 2979, 2905 and 2812 cm^{-1}. A strong peak observed around 1697 cm^{-1} is due to the out of plane bending of N-H vibration of the molecule. An absorption peak at 1605 cm^{-1} is due to carbonyl stretching (C=O) of the molecule. In plane bending of N-H stretching is observed at 1527 cm^{-1}.

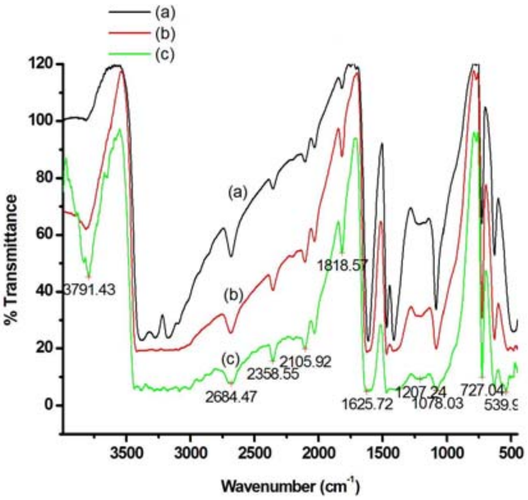

Fig. 5 FT- IR Spectra of CTC and doped CTC Crystals [(a) Cu Thiourea complex, (b) L-Glutamic acid doped Cu Thiourea complex and (c) L-Valine doped Copper Thiourea]

The absorption peaks at 1482 and 1443 cm^{-1} are due to skeletal vibrations of aromatic ring. Out-of-plane bending vibration modes of aromatic C–H bonds are observed at 1367, 1280, 1182, 1113 and 1012 cm^{-1}. The absorption peaks observed below 1000 cm^{-1} illustrates in-plane-bending vibration modes of C–H bonds. From this spectroscopic investigation, the presence of all the fundamental functional groups of the grown sample was confirmed qualitatively. Moreover, no absorption peaks related to the solvent molecules or any other impurities were observed which confirms the absence of solvent trapping in the crystal lattice and also the purity of the grown sample.

Table: 1 Observed and Calculated IR frequencies (cm^{-1}) of Cu Thiourea complex and Cu Thiourea complex doped with L-Glutamic acid and L-Valine

Species	Calculated frequencies (cm^{-1})	Observed IR frequencies and intensities			
		Cu Thiourea complex	Cu Thiourea complex doped with L-Glutamic	Cu Thiourea complex doped with L-Valine	Assignments
A/E	3791	3790 (w)	3785 (broad)	3789 (Broad)	NH_2 Asymmetric Stretching in phase
	3425	3430 (vw)	3439 (vw)	3435 (vw)	NH_2 Asymmetric Stretching out of phase
	3375	3371 (vw)	3369 (VW)	3366 (vw)	NH_2 Symmetric Stretching in phase
	3295	3290 (vw)	3286 (vw)	3285 (vw)	NH_2 Symmetric Stretching out of phase
	3225	3222 (vw)	3220 (vw)	3220 (vw)	C-H Stretching
	3175	3174 (w)	3170 (vw)	3165 (vw)	N-H Asymmetric Stretching in phase
	3090	3085 (vw)	3083 (vw)	3081 (vw)	N-H Asymmetric Stretching out of phase
	2875	2873 (vw)	2870 (vw)	2868 (vw)	N-H Symmetric Stretching in phase
	2684	2682 (m)	2680 (m)	2678 (m)	N-H Symmetric Stretching out of phase
	2359	2359 (m)	2352 (w)	2350 (w)	Overtone/combination
	2315	2313 (w)	2315 (w)	2315 (w)	Overtone/combination
	2107	2105 (w)	2104 (w)	2103 (w)	Overtone/combination
	2010	2009 (w)	2006 (w)	2003 (w)	Overtone/combination
	1820	1819 (w)	1815 (w)	1813 (w)	NH_2 Deformation
	1626	1625 (vs)	1623 (vs)	1622 (vs)	C-NH_2 Asymmetric Stretching
	1450	1449 (vw)	1445 (vw)	1444 (vs)	C-NH_2 Symmetric Stretching
	1375	1373 (w)	1371 (w)	13 69 (w)	NH_2 Rocking in phase
	1210	1207 (m)	1205 (m)	1203 (m)	NH_2 Rocking out of phase
	1078	1084 (s)	1079 (s)	1075 (s)	NH_2 Twisting
	800	800 (vw)	799 (vw)	799 (vw)	CN Stretching
	725	728 (s)	726 (s)	725 (s)	N-C-N Deformation /CS Stretching
	650	645 (vw)	644 (vw)	643 (vw)	NH_2 Torsion/π N_2CS out of plane
	600	599 (vw)	598 (vw)	597 (vw)	N-C-N Deformation/NH_2 Wagging
	575	574 (vw)	574 (vw)	574 (vw)	CS Deformation/Wagging
	539	538 (w)	536 (w)	535 (w)	N_2CS Deformation out of plane
	475	478 (s)	477 (s)	475 (s)	NH_2 Deformation

5. Thermal studies

Fig. 6(a) illustrates the Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) curves for the grown copper-thiourea complex doped CTC crystal. The DTA curve implies that the material undergoes an irreversible endothermic transition at 200°C where the melting begins. This peak was endothermic peak, represents the temperature at which the melting terminates which corresponds to its melting point at 210°C.

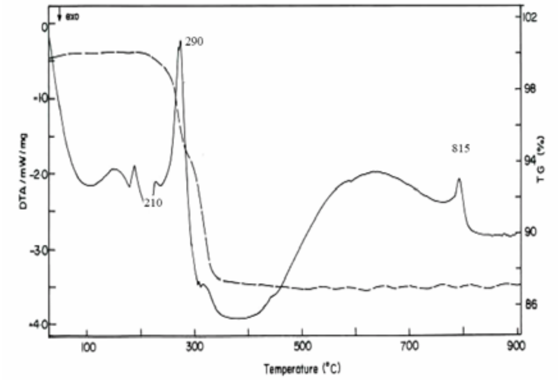

Fig. 6(a) TGA-DTA curves of L-Glutamic acid doped Copper Thiourea Complex Crystal.

Ideally, the melting point of the trace corresponds to a vertical line. The sharpness of the endothermic peak shows good degree of crystallinity of the grown ingot. The exothermic peak at 290°C indicates a phase change from liquid to vapour state as evident from the loss of weight of about 87% in TG curve.

The results suggested that the phase stability of the L-Valine doped CTC might have been improved when compared to the pure CTC sample that results in a higher decomposition temperature. The total mass loss is 2.774% and comparable to pure CTC sample contrary to the above results, the L-Glutamic acid doped CTC sample do not show any splitting in the major DTA peak at least up to the resolution limit of the instrument. It can be noticed that the intensity of satellite peak (227°C) is very less when compared to other two samples. This result is very significant in two different aspects (i) the result indicates that the dopant L-Glutamic acid is actually substituted in the crystal lattice. (ii) The result suggests the CTC phase stability improved in the presence of L-Valine. However, further studies with various doping level is required for conforming their observations. The TGA result is similar to other two samples with a load mass loss of 2.699%. Fig.4 (a) shows that loss of water molecule occurs at 150°C, it is exothermic reaction and at 274.6°C crystallization of salt occurs. At 380°C loss of CO_2 molecule which is exothermic reaction. The TGA–DTA spectra of amino acid (L-Valine) doped CTC crystal is shown in the Fig.6(b).

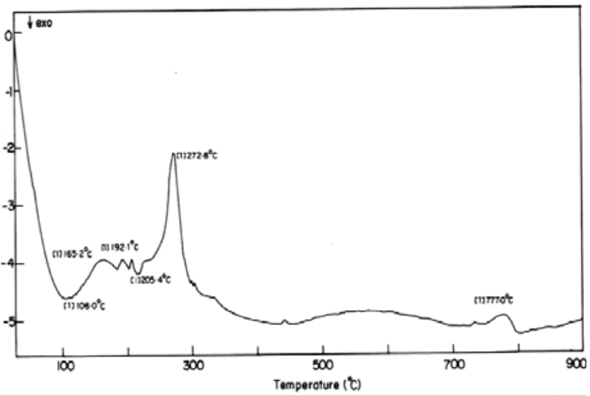

Fig. 6(b) TGA-DTA spectra of amino acid (L-valine) doped CTC crystal.

6. Hardness measurements

The Vickers hardness number were calculated using the relation

$$H_v = 1.8544p / d^2 \quad kg\text{-}mm^{-2}$$

Where p is the applied load in kg and d is the diagonal length of the indentation mark in mm. Hardness values are always measured from the observed size of the impression remaining after a loaded indenter has penetrated and has been removed from the surface. Thus, the observed hardness behaviour is the summation of a number of effects involved in the material's response to the indentation pressure during loading, in the final measurement of the residual impression. The hardness measurements were made using the Vickers pyramidal indentor for various loads. The maximum value of hardness for cleavage plane of CTC crystal is found to be 287.24 kg/mm^2. Addition of impurities in CTC extensively modifies the hardness values and the doped CTC crystals are much harder than the pure crystal. The hardness values of the pure and doped CTC crystals are tabulated in Table 2.

Table 2. Microhardness values of pure and doped CTC Crystals

S.No	Crystal	Microhardness (kg/mm^2)
1.	Pure CTC	225.79
2.	L-Glutamic acid doped CTC	168.67
3.	L-Valine doped CTC	287.24

7. NLO properties

Measurements were made using the Kurtz and Perry powder method. Schematic representation of the SHG setup is shown in Fig. 7. Approximately 50 mg of material was loaded into the sample cell, which was formed between two Pyrex 25X75X1 mm microscope slides (Can lab). Two strips of masking tape with a 2 cm diameter hole cut through the center were placed 3 cm from the end of one of the slides. The circular window was filled with a thin layer of sample (0.3 mm thick). The second microscope slide was clipped onto the first, sandwiching the sample between the slides. The 1064 nm fundamental output from a Q-switched Nd: YAG laser (Quanta Ray) was divided by a beam splitter, where one portion of the light was directed onto a reference cell containing CTC and doped CTC. The resultant second-harmonic signal (532 nm) was passed through a sharp-cut filter (Corning 527) designed to eliminate any stray visible light from the laser flash lamp, and several neutral density filters (Wratten, 0.3 + 0.7) designed to attenuate the second-harmonic signal, before being focused onto a photomultiplier tube (RCA IP28). The second portion of the fundamental beam was directed on to a second cell containing the sample to be measured. Any second-harmonic produced was passed through a series of neutral density filters (Wratten, 1.0 + 0.7), then focused into a monochromator (Beckman DU spectrophotometer, model 2400) in order to discriminate between SHG light and stray visible light and IR light. Monochromatic 532 nm light was then directed on to a second photomultiplier (RCA IP28) for measurement.

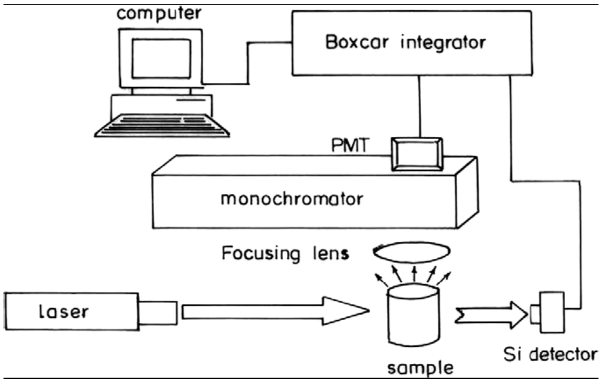

Fig.7 SHG set up

In order to measure the SHG efficiency of a given material accurately, urea was used as reference material. In order to confirm the NLO property the doped CTC crystal has been tested using the Nd–YAG laser. Small crystals of amino acids doped CTC was placed on the sample holder and the red color laser beam was made to pass through the crystal and the incoming beam passing through the crystal converted into the green light. The efficiency of doped CTC crystals were compared with pure CTC and also show that L-Valine doped CTC crystal has higher efficiency. Observing the green signal from the powdered doped CTC sample and the power of the SH signal is relatively higher (1.5 times) than that of pure CTC. Further investigations on phase matching studies of the grown crystal are under progress and the outcome will be published elsewhere.

8. Conclusions

Pure and amino acids (L-Glutamic acid, L-Valine) doped Copper Thiourea complex crystals were grown by slow solvent evaporation technique using solvent of water. Various functional groups present in the grown crystal were identified by FTIR spectroscopy. Thermal stability of the grown sample was studied by TG&DTA analysis. TG curve of this sample indicates that the crystalline sample has a melting point 64°C and chemically stable up to 150°C. Mechanical properties of the grown crystal were analyzed by micro hardness studies. The doped crystals Copper Thiourea Complex undergo two-stage thermal decomposition similar to that of pure ones. The micro hardness studies of doped CTC crystals were analyzed.

The Nonlinear Optical studies analyzed with Nd–YAG laser technique confirm that the grown crystals are non-linear in nature. Doped crystals have relatively higher hardness values than the pure crystals. Powder X-Ray Diffraction analysis confirms the structure and change in lattice parameter values for the doped crystals. The presence of dopants in the crystal lattice has been qualitatively confirmed by Fourier Transform Infrared analysis. The sharp absorption onset at 340 nm and the high transmission of the grown crystal at wavelength above 400 nm exhibit the optical quality, low concentration of grown-in defects and suitability for optical applications as well. The material CTC shows high SHG efficiency than that of KDP and hence it could be applicable for nonlinear optical applications.

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