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Research Article

INVESTIGATION ON VARIOUS STUDIES OF THIOUREA DOPED L-ALANINE CADMIUM CHLORIDE CRYSTALS M. Malathi¹, P.Selvarajan², U.Rajesh Kannan³

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ABSTRACT

The growth of L-alanine cadmium chloride (LACC) crystals was carried out by solution method with slow evaporation technique. Nucleation kinetic studies were performed for the samples to understand the nucleation process. The grown crystals were subjected to structural, mechanical, thermal, electrical and spectral properties. FTIR and ultra violet – visible (UV-Vis) spectral studies have been carried out to find the suitability of the grown crystals for device fabrication. AC conductivity values of the samples were measured using an LCR meter at different frequencies and temperature. Activation energy has been calculated for all the samples. The mechanical parameters like work hardening coefficient, stiffness constant and yield strength of the samples have been determined. Third order nonlinear parameters like nonlinear refractive index, nonlinear absorption and third order susceptibility were determined by Z-scan technique for pure and doped samples of LACC.

Keywords: LACC complex, FTIR, UV, AC conductivity, NLO

1. INTRODUCTION

An amino acid mainly contains a carboxylic group and an amino group and forms the building blocks of the protein structure. In this work amino acid *i.e.* L-alanine has been considered to prepare thiourea doped L-alanine cadmium chloride crystals. L-alanine is a nonessential amino acid which can be manufactured by the human body, and does not need to be obtained directly through the diet. Among the amino acids, L-alanine is the simplest acentric crystal and it is a naturally occurring chiral amino acid [1, 2]. Efforts have been made on the amino acid mixed complex crystals in order to make them suitable for linear and nonlinear device applications. In amino acid based metal organic complexes, the organic ligand is usually more dominant in the NLO effect. As for the metallic part, focus is on the metals like Zn, Cd and Hg as these compounds usually have a high transparency in the UV region, because of their closed d¹⁰ shell. Potential NLO materials like bisthiourea cadmium chloride (BTCC), triallylthiourea cadmium chloride (TATCC) have been studied. The amino acids like L-arginine and Lhistidine have been exploited for the formation of salts with different organic/ inorganic acids.

As a result, semi-organic NLO materials such as Larginine phosphate monohydrate, L-histidinetetrafluroborate have been synthesized and are found to be suitable in number of NLO applications [3, 4]. Several new complexes incorporating the amino acid L-alanine have been recently crystallized and their structural, optical and thermal properties have been investigated [5-8]. Lalanine cadmium chloride was first synthesized by Kathleen et al. [9] and later its properties were studied by Dhanuskodi et al. [10]. Bright et al. have reported the frequency and temperature dependence of dielectric properties of L-alanine cadmium chloride [11]. Linear and nonlinear optical properties of L-alanine cadmium chloride were studied by Kalaiselvi et al. [12] with varieties of dopants. To improve the various physical and chemical properties of LACC crystals, thiourea has been added as the dopant in this work. The aim of the work is to grow thiourea doped L-alanine cadmium chloride (LACC) crystals and to subject the grown crystals to various studies such as nucleation kinetic studies, UVvisible transmittance studies, FTIR studies and NLO studies.

2. EXPERIMENTAL

L-alanine (99% purity) and analar grade cadmium chloride monohydrate were purchased commercially and they were taken in 1:1 molar ratio to prepare L-alanine cadmium chloride (LACC) salt. The solvent used here is double distilled water. The dissolved saturated solution was heated at 55°C for the synthesis of LACC salt. To obtain the thiourea doped LACC salts, 5 wt%, 10 wt% and 15 wt% of thiourea was added into the solutions of L-alanine cadmium chloride separately. Single crystals of undoped and thiourea doped LACC were grown by solution method with slow evaporation technique using the saturated solutions of the relevant synthesized salts. The saturated solutions of the salts were stirred well and were filtered and taken in four beakers separately for crystallization. After a period of 30-35 days, crystals were harvested and used for characterization studies. UV-visible transmittance spectra of the grown crystals were recorded using a Varian Cary 5E UV-vis spectrophotometer in the range 190-1100nm. The FTIR spectra of pure and doped crystals were recorded employing a Perkin-Elmer spectrometer in the form of solid dispersed in KBr pellet technique. In this work, the melting point apparatus (MAKE: TEMPO) was used to find the thermal stability of the samples. The third-order nonlinear optical properties of a crystal are characterized by the Z-scan technique.

3. RESULTS AND DISCUSSIONS

3.1. UV-visible transmittance spectra

UV-visible transmittance spectra are attributed to a process in which the electrons of atoms or molecules absorb radiant energy and undergo transitions to higher energy levels. The wavelength at which ultraviolet absorbance maximum is found and it depends upon the magnitude of the energy involved for a specific electronic transition. UV-visible transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range 200-1100 nm. A crystal of thickness of about 1.5 mm has been used in this study. The transmittance spectra of thiourea doped LACC crystals and the samples show the sufficient transmittance in the visible region. The optical transmittance of LACC crystals is reduced when they are doped with thiourea and it depends on the concentration of dopant. The cut-off wavelength is observed to be around 235-238 nm for thiourea doped LACC crystals and this corresponds to the fundamental absorption of the samples.

The grown crystals of this work have low absorption, sufficient and excellent transmittance in the entire visible and near infrared region of the UV-visible spectra and hence they are useful in nonlinear optical applications. The optical band gap values of the samples have been determined using the formula E_g (in eV) = 1240/ λ where λ is the cut-off wavelength. Optical band gap for the grown crystals are observed to be high and hence the grown crystals are useful for SHG generation devices and opto-electronic devices [13].



Fig 1: UV-visible transmittance spectra of undoped and thiourea doped LACC crystals

Table 1: Values of optical band gap for pure anddoped crystalline samples

Sample	Band gap (eV)
L- alanine cadmium chloride (LACC)	5.21
LACC + 5 wt% of thiourea (LACCT5)	5.23
LACC + 10 wt% of thiourea (LACCT10)	5.25
LACC + 15 wt% of thiourea (LACCT15)	5.28

Linear optical constants such as reflectance, refractive index and the extinction coefficient at cut-off wavelength and maximum wavelength (1100 nm) are given in table 2.

When L-alanine cadmium chloride (LACC) crystals are doped with thiourea, the reflectance values are observed to be increased with the increase of doping concentration. The refractive index values are found to obey the Cauchy's formula in the visible region of the spectrum. The grown samples have low extinction coefficient and it confirms that the grown materials are suitable for optoelectronic device applications.

Sample	Reflectance at Refractive index a		tive index at	Extinction coefficient x10 ⁻⁵ at		
Sample	$\lambda_{\rm cutoff}$	λ_{\max}	$\lambda_{\mathrm{cutoff}}$	λ_{\max}	$\lambda_{\mathrm{cutoff}}$	λ_{\max}
LACC	0.21	0.14	1.95	1.76	10.23	2.37
LACCT5	0.23	0.11	1.99	1.69	9.95	2.12
LACCT10	0.28	0.15	2.48	1.78	10.34	2.37
LACCT15	0.30	0.18	2.17	1.90	11.86	2.65

Table 2: Linear optical constants of the grown crystals (λ_{max} =1100 nm)

3.2. Fourier Transform infrared (FTIR) studies

An infrared spectrum represents absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms. Fourier transform IR spectrum of pure and doped crystals were recorded in the range 100 to 400 cm⁻¹ employing a Perkin-Elmer spectrometer in the form of solid dispersed in KBr pellet technique. The FTIR spectra of pure and doped LACC crystals were recorded and various assignments related to the vibrational frequencies of the functional groups have been identified. The FTIR spectra of the samples are shown in the figures 2 and 3.



Fig.2: FTIR spectrum of pure L-alanine cadmium chloride (LACC) Sample

From the results, it is observed that NH_2 groups of Lalanine and L-proline molecules in the samples are protonated by COOH group giving rise to NH_3^+ , the broad envelope in the higher wave number region between 3400 and 2900 cm⁻¹ and it was due to hydrogen interaction with other atoms such as N–H stretching of NH_2 , OH stretching and C–H stretching. In the samples, the carboxylic acid group is present as carboxylate ion and amine group exists as ammonium ion.



Fig.3: FTIR spectrum of LACC crystal doped with 15 wt% of thiourea

Table 3: FTIR Spectral assignments for LACCcrystal doped with 15wt% of thiourea

Wave number(cm ⁻¹)	Assignments
3338	NH ₃ ⁺ asymmetric stretching
3059	NH ₃ ⁺ symmetric stretching
2677	Combination band
2574	CH ₂ stretching
1620	NH ₃ ⁺ deformation
1427	COO ⁻ stretching
1342	C-C bending
1117	NH ₃ ⁺ rocking
998	CCN stretching
648	COO ⁻ scissoring
565	COO ⁻ rocking
488	$\rm NH_3^+$ torsion

This is the zwitterionic nature of the samples. The functional groups such as NH_3^+ , OH, COO⁻, CH₂, CCN, C-C etc present in the samples have been identified [14,15]. The spectra of the samples are similar

except some absorption peaks/bands are slightly shifted or broadened due to doping of thiourea into LACC samples. The spectral assignments to the bands/peaks of the FTIR spectra of the samples are provided in the table 3.

3.3. Determination of AC conductivity

Using the data of dielectric constant and dielectric loss in the table 4, AC electrical conductivity of a crystal was calculated using the formula $\sigma_{ac} = 2\pi f \epsilon_0 \epsilon_r \tan \delta$ where ε_{0} is the permittivity of free space, ε_{r} is the dielectric constant of the sample, $\tan \delta$ is the dielectric loss of the sample and f is the frequency of AC signal. The calculated values of AC conductivity for the samples at different frequencies at 30 °C are given in the table 4. The AC conductivity is directly proportional to dielectric constant and dielectric loss and hence the same behavior is noticed in the case of AC conductivity. The presence of impurities and vacancies is responsible for the alteration of the values of AC conductivity. The defect will concentration increase exponentially with temperature and consequently the AC conductivity increases.

It is observed from the results that the conductivity values increase for thiourea doped LACC crystals and this is due to increase of dielectric constant and loss factor as the samples are doped. Doping of LACC and with the organic dopant like thiourea leads to increase of the charged carriers and hence the conductivity increases for the doped samples of this work.



Fig. 4: Plots of AC Conductivity versus temperature for thiourea doped LACC crystals at 10³Hz

Frequency(Hz)	Dielectric Constant	Dielectric Loss	AC Conductivity (Ω m) ⁻¹ ×10 ⁻⁷
100	11.45	0.85	0.540
500	10.46	0.74	2.150
1000	9.98	0.63	3.494
5000	9.34	0.55	14.27
104	8.37	0.46	213.9
10^{5}	7.35	0.39	1593.1
10^{6}	6.58	0.31	1133.6

Table 4: Values of AC conductivity for LACC crystal doped with 15 wt% of thiourea

3.4. Mechanical studies

The microhardness is related to yield strength (σ_y) by the equation Hv = 3 σ_y . The yield strength is defined as the stress at which a predetermined amount of permanent deformation occurs. Since the work hardening coefficient 'n' is found to be more than 2, yield strength of the material can be found out using the relation Yield strength (σ_y) = (H_v/3) (0.1)ⁿ⁻² where σ_y is the yield strength and H_vis the hardness of the material [16]. The elastic stiffness constant (C₁₁) for different loads was calculated using Wooster's empirical formula C₁₁ = H_v^{7/4}. The calculated values of yield strength and stiffness constant of the pure and doped LACC crystals are provided in the tables 5 and 6. As the results of hardness,

the yield strength and stiffness of the samples are found to be increasing with increase of the applied load. The stiffness constant with the load for samples gives an idea about the measure of resistance of plastic to bending and tightness of bonding between neighboring atoms. It was observed that the stiffness constants increase with increase of load for the grown crystals. The addition impurity or dopant has the prominent effect on hardness, yield strength and stiffness constant. When dopants are introduced into the host crystals like LACC, the defects act as the obstacles to dislocation motion, therefore, the mechanical parameters like hardness, yield strength and stiffness constant of the samples are found to increase with increase of doping concentration.

Load	Values of yield strength ×10 ⁶ in pascals for			
(grams)	LACC + 5wt% of thiourea	LACC + 10wt% of thiourea	LACC + 15wt% of thiourea	
25	120.6	111.1	104.5	
50	133.9	124.1	114.3	
75	169.8	147.0	133.9	
100	205.8	182.9	166.6	

Table 5: Values of yield strength for thiourea doped L-alanine cadmium chloride crystals

Table 6: Values of stiffness constant for thiourea doped L-alanine cadmium chloride crystals

Load	Values of stiffness constant ×10 ¹⁴ in pascals for			
(grams)	LACC + 5wt% of thiourea	LACC + 10wt% of thiourea	LACC + 15wt% of thiourea	
25	9.491	8.22	7.386	
50	11.39	9.97	8.640	
75	17.27	13.42	11.39	
100	24.18	19.67	16.71	

Table 7: Values of melting point/decomposition point of the samples

Sample	Melting point/decomposition point
L-alanine cadmium chloride(LACC)	107°C
LACC + 5wt% of thiourea (LACCT5)	106°C
LACC + 10wt% of thiourea (LACCT10)	104°C
LACC +15wt% of thiourea (LACCT15)	103°C

3.5. Measurement of melting point/ decomposition point

The melting point or decomposition point of a sample can be measured by using a melting point apparatus. In this work, the melting point apparatus (Make: TEMPO) was used to find the thermal stability of the samples. The measured values of melting point/decomposition point of the samples are given in the table 7. The melting point of pure LACC crystal is found to be 107°C and that of pure of LPCC crystal is 205°C and these values are observed to be in close agreement with the reported values. From the results, it is observed that the melting point values of thiourea doped LACC crystals are more than that of pure LACC crystal. The increase in melting point is due to increase in hardness of doped LACC crystals as observed in the microhardness studies.

3.6. Z- scan Studies

Measurements of the normalized transmittance by varying the sample position (Z) have been made for the grown crystals in open and closed aperture modes. The open aperture and closed aperture curves for the samples of undoped LACC and thiourea doped LACC (10 wt%) crystals are given in the figure 5.In Z-scan method, He-Ne laser ($\lambda = 632.8$ nm) was used as the light source and focused by a lens of 22.5 cm focal length. The obtained values of third-order NLO parameters are given in the table 8.

Table 8: Third-order NLO parameters of the sample

Sample	Nonlinear refractive index(n ₂)×10 ⁻¹⁰ (cm ² /W)	Nonlinear absorption coefficient (β)x 10 ⁻⁵ (cm/W)	Third-order nonlinear susceptibility (X ⁽³⁾)x 10 ⁻⁶ (esu)
LACC	5.463	7.451	4.870
LACCT10	3.156	4.873	2.765



Fig 5: Open aperture and closed aperture Z-scan curves for thiourea doped LACC sample

The results show that the values of nonlinear refractive index (n_2) , the nonlinear absorption coefficient (β) and third-order nonlinear susceptibility ($\chi^{(3)}$) of the thiourea doped LACC crystal are less compared to those of their undoped host crystals. Due to inclusion of dopants in the interstitials of the LACC crystals, the values of thirdorder NLO parameters have been changed. The results of nonlinear absorption and nonlinear refraction of the samples reveal that these phenomena always coexist as they result from the same physical mechanisms. This study helps to find the materials for optical switching and sensor protection applications in connection with both nonlinear absorption and nonlinear refraction and to understand the third-order NLO phenomena [17, 18].

4. CONCLUSIONS

Pure and thiourea doped L-alanine cadmium chloride crystals were grown by slow evaporation technique at room temperature. UV-visible transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range 200-1100 nm. From the transmittance spectra, it is noticed that pure and doped LACC crystals have good transparency in visible region and hence they are useful in nonlinear optical applications. Linear optical constants such as reflectance (R), refractive index (n) and extinction coefficient (k) were determined from the data of optical transmittance. Fourier transform IR spectra of pure and doped LACC and LPCC crystals were recorded and the functional groups such as NH_3^+ , OH, COO, CH_2 , CCN, C-C etc present in the samples have been identified by FTIR studies. It is found that the conductivity values increase for thiourea doped LACC crystals and this is due

to increase of dielectric constant and loss factor as the samples are doped. The mechanical parameters like hardness, yield strength and stiffness constant of the samples are found to increase with increase of doping concentration. The mechanical parameters like hardness, work hardening coefficient, stiffness constant and yield strength of the samples have been determined. Third order nonlinear parameters like nonlinear refractive index, nonlinear absorption and third order susceptibility were found by Z-scan technique for pure and doped samples of LACC.

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6. REFERENCES

- 1. Razzetti C, Ardoino M, Zanotti L, et.al, Cryst. Res., Technol, 2002; 37:456-465.
- 2. Eimerl D, Velsko S, Davis L, et.al J. Quantum Electron, 1989; 25:179.
- 3. Dhanuskodi S, Ramajothi J, et.al, Cryst. Res. Technol., 2004; 39:592.
- 4. Babu DR, Jayaraman D, Kumar RM, et.al. Crystal Growth, 2002; 245:121.

- 5. Mohan Kumar R, Rajan Babu D, Jayaraman D, Jayavel R, et.al, *J. Crystal Growth*, 2005; **275:**1935.
- 6. Justin Raj C, Jerome Das S, et.al. *J.Crystal Growth*, 2007; **304:**191.
- 7. J.Lucia Rose AS, Selvarajan P, Perumal S, et.al *Physica*, 2011; **406:** 412
- Kathleen I. Schaffers, Douglas A, Keszler et al. Acta Cryst.C, 1993; 49:1156.
- 9. Dhanushkodi S, Vasantha K, Angeli Mary PA, et.al, *Specrochim. Acta. Part A*, 2007; **66:** 637.
- 10. Bright KC, Freeda TH, et.al, *Physics B*, 2010; **405:**3857.
- 11. Kalaiselvi P, Alfred Cecil Raja S, Vijayan N, et al. *Optik*, 2013; **124:** 6978.

- 12. Lucia Rose AS, Selvarajan P, Perumal S et al. *Physica B*, 2011; **406**:412-417.
- Nagamoto K. IR and Raman Spectra of Inorganic and coordination compounds, John Wiley and Sons New York, 1978.
- 14. Socrates G. Infrared Characteristic Group Frequencies, Wiley-Interscience Chichester, 1980.
- 15. Anandha Babu G, Ramasamy, P et.al, Materials Chemistry and Physics, 2009; 113; 228.
- 16. Wooster WA. Rep. Prog. Phys, 1953; 16:62-82.
- 17. Xia, T, Hagan DJ, Sheik-Bahae M et al. *Opt. Lett*, 1994; **19**:317-319.
- 18. Bube RH, *Photoconductivity of solids*, Wiley, New York, 1981.