



Article Title: Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

Jaslin J Christopher¹, A. S. Jebamalar², J. Beena³

¹Assistant Professor, Department of Chemistry, Govt. Arts and Science College, Palkulam, Kanyakumari, Tamilnadu, India - 629401

²Assistant Professor, Department of Physics & Research Centre, Nesamony Memorial Christian College, Marthandam, Tamilnadu, India - 629165

³Research Scholar, Department of Physics & Research Centre, Nesamony Memorial Christian College, Marthandam, Tamilnadu, India - 629165

*jaslinchris@gmail.com

ABSTRACT

Pure and thiourea doped single crystals of L-proline cadmium chloride monohydrate were grown by slow evaporation method at room temperature. The SXRD analysis gives the details about the lattice parameters and crystal system. EDAX spectrum corroborated the incorporation of C, H, S, Cd, Cl in doped single crystal. FTIR analysis confirms the presence of various functional groups in the title material. The UV transmittance spectrum confirms the increase in transparency of the doped crystal. The green light emission of the title material was attributed by fluorescence analysis. The mechanical analysis suggests that thiourea doped L-Proline cadmium chloride monohydrate comes under soft material category and the second harmonic efficiency of doped crystal was 0.8 times than KDP.

Keywords: single crystal; SXRD; optical material; doped crystal; SHG

1 Introduction

In recent years the need for high-performance materials suitable for device fabrication highly increases the progress towards crystal technology and its applications [1]. The science of crystal growth indeed catapulted the demand for solid state materials which finds applications in semiconductor industries, data processing, imaging, electronics, computer and photonics [2]. Semi-organic materials have the potential for combining high optical nonlinearity and chemical flexibility of organic with the high physical strength of inorganic. One approach to organic-based NLO materials in semi organic class is to form compounds in which a polarizable organic molecule is stoichiometric ally bonded to an inorganic host. Amino acids and their complexes belong to a family of organic materials that have potential applications in frequency conversion [3]. L-proline cadmium chloride monohydrate (LPCCM) is one such semi-organic material crystallizing in the crystal form of orthorhombic crystal system with space group $P2_12_12_1$. Synthesis, growth, Powder XRD, UV-Vis, SHG efficiency studies were reported by the authors of reference [4, 5, 6] on LPCCM crystals. Within the scope of our literature survey, no work has been reported on the modification of optical properties of L-PCCM by using butter



Article Title: Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

of thiourea as dopant. Thiourea doped LPCCM single crystals were grown by slow evaporation method and analysed using various analysis.

2 Experimental Procedure

2.1 Synthesis

Pure L-proline cadmium chloride (LPCC) crystal was prepared by the reaction of L-proline and Cadmium chloride monohydrate. De-ionized water was used as a solvent. L-proline (LR grade) and cadmium chloride monohydrate (AR grade) were taken in 1:1 ratio and it is dissolved in de-ionized water. The prepared solution was stirred well to 4 hours to attain homogeneity. Similarly, the saturated solution of L-proline and cadmium chloride monohydrate was prepared and 1mole% of thiourea was doped in the solution and stirred well to 4 hours. The solution was maintained at room temperature for evaporation. After 10 days good quality crystals were harvested. Fig. 1(a) and 1(b) depicts the photography of the grown pure and thiourea doped LPCCM crystals.



Figure 1(a) and 1(b): Pure and Thiourea doped LPCCM

2.2 Characterization techniques

The lattice parameters of the synthesized PTSC single crystal were obtained by using Bruker kappa APEXII single crystal X-ray diffract meter with $\text{MoK}\alpha$ ($\lambda = 0.7107 \text{ \AA}$) radiation. FTIR spectrum of the PTSC was acquired using Perkin Elmer-spectrum II spectrophotometer and UV-Visible transmittance spectrum was recorded with the help of Perkin Elmer Lambda 35 spectrophotometer in the range of 200 nm – 1100 nm. Micro hardness measurement has been done by using shimadzu HMV – 2T testing device with an indenter utilizing a diamond pyramid.



Article Title: Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

3 Results and Discussions

3.1 Single Crystal XRD

The single crystal X-ray diffraction analysis lucubrates that pure and Thiourea doped LPCCM single crystal belongs to orthorhombic system with non-Centro symmetric space group $P2_12_12_1$ and the lattice parameters of the synthesized material was portrayed in table 1. The crystallographic data of the pure material agrees with the reported literature [4].

Table 1: Single crystal XRD analysis data.

Crystal	Pure LPCCM	Thiourea doped LPCCNM
Crystal system	Orthorhombic	Orthorhombic
a (Å)	7.32	7.30
b (Å)	10.03	10.01
c (Å)	13.56	13.54
$\alpha=\beta=\gamma$	90	90
V(Å ³)	996	990

3.2 FTIR analysis

FTIR Spectral analysis corroborated the functional groups present in the material and fig. 2 (a) and fig. 2 (b) denotes the FTIR spectrum of pure and doped title material. The small variations in the doped FTIR spectrum ensures the incorporation of thiourea in the title material. In the spectra the peaks at 3502 cm^{-1} and 3503 cm^{-1} were assigned to the O-H stretching vibration of H_2O [4,6]. The peak at 3131 cm^{-1} and 3131.49 are corresponds to NH Stretching Vibration. The existence of the COO^- ion in zwitterionic form is determined by the lack of any strong IR band at 1700 cm^{-1} .

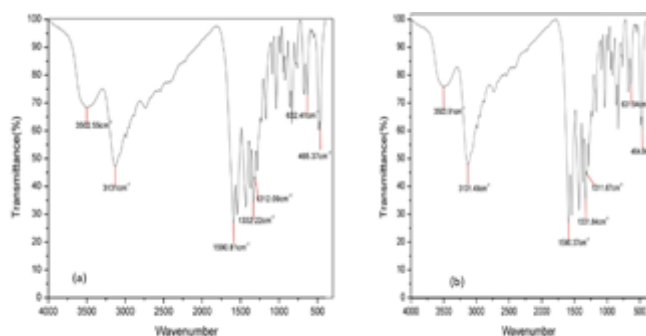


Figure 2(a) and 2(b): FTIR spectrum of Pure and Doped LPCCM



Article Title: Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

3.3 Energy dispersive X ray analysis (EDAX)

The EDAX spectrum of the grown thiourea doped LPCCM single crystal depicted in fig. 3 and the presence of carbon, oxygen and sulphur in the spectrum confirms the incorporation of thiourea in the grown crystal.

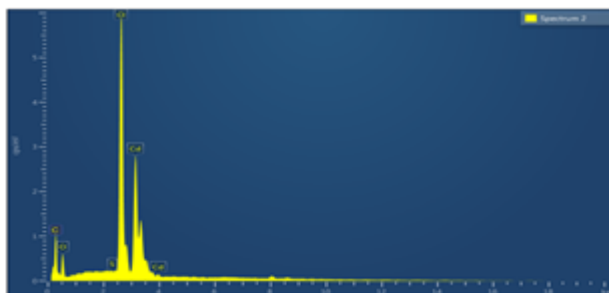


Figure 3: EDAX spectrum of Doped LPCCM

3.4 UV- VIS spectroscopy

The recorded spectra of pure LPCCM and thiourea doped LPCCM single crystals were shown in fig. 4(a) and 4(b). Thiourea doped LPCCM crystals shows 80% transmittance, whereas pure LPCCM crystals show 70% transmittance. It has been observed that the thiourea doped crystals have the lower cut of wavelength at 239 nm and the pure crystals shows the lower cut off wavelength at 237 nm with the optical band gap 5.19 eV and 5.24eV.

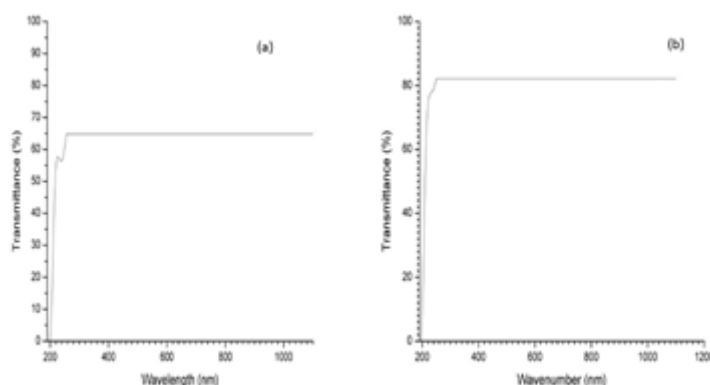


Figure 4(a) and 4(b): UV transmittance spectrum of Pure and Doped LPCCM

3.5 Fluorescence Analysis

The emission spectrum of thiourea doped LPCCM divulges that crystal was excited with wave length 237 nm and the emission peak was observed at 531 nm. This peak indicates the grown crystal has a green fluorescence emission [6-8]. The emission spectrum of thiourea doped LPCCM shown in the fig. 5. This shows that the crystal can be used in the long pass optical filters. The sharp peak indicates its good crystallinity [9].



Article Title: Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

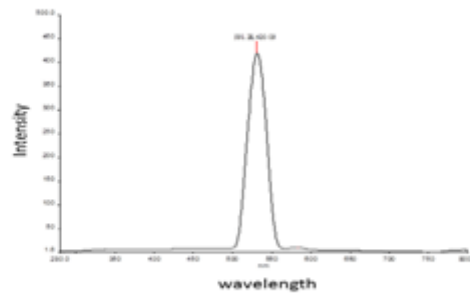


Figure 5: *Fluorescence spectrum of Doped LPCCM*

3.6 Mechanical analysis

The variation of micro hardness with applied load P and variation of $\log d$ vs. $\log P$ were shown in fig. 6(a) and 6(b). The hardness H_V increases with the applied load known as reverse indentation size effect (RISE) [10-12]. The work hardening coefficient of the grown crystal has been calculated from the slope of $\log p$ and $\log d$ graph. The n value obtained for thiourea doped LPCCM single crystal is 3.5. This shows that the grown crystal belongs to soft material category [13, 14].

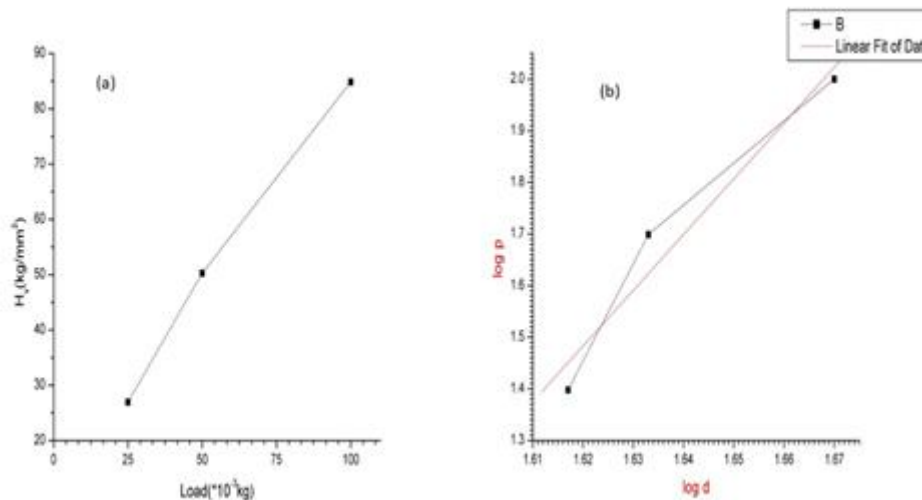


Figure 6(a) and 6(b): *Hv with load P and $\log d$ vs. $\log p$ plot*

3.7 Second Harmonic Generation

The second harmonic generation efficiency of the grown material was estimated to corroborate the nonlinear optical property of the material. Q switched high energy Nd: YAG laser with wavelength 1064 nm was used to estimate the SHG efficiency. During the experiment the



Article Title: Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

sample thiourea doped LPCCM emits green light which confirms the NLO property of the material. The SHG efficiency of title material was 0.8 times that of KDP [6, 8, 15].

4 Conclusion

Pure and thiourea doped single crystals of L Proline cadmium chloride monohydrate single crystal were grown by slow evaporation method at ambient temperature. The SXRD analysis reveals that the crystal belongs orthorhombic crystal system with centro-symmetric space group. FTIR analysis confirms the various functional groups present in the title material. EDAX spectrum corroborated the presence of C, H, S, Cd, Cl in doped material. The UV transmittance spectrum confirms the increase in transparency from 70% to 80% due to thiourea doping. The green light emission of the title material was attributed by fluorescence analysis. The mechanical analysis suggests that thiourea doped LPCCM comes under soft material category and the second harmonic efficiency of title material was 0.8 times than KDP. The obtained results concludes that thiourea doped LPCCM was a potential material for Photonics device fabrication.

Acknowledgement

The authors like to thank B. S. Abdur Rahman Crescent Institute of Science and Technology, Archbishop Casimir Instrumentation Centre (ACIC) and SAIF - IIT Madras for providing instrumentation facilities.

Reference

1. D. Sivavishnu; R. Srineevasan; J. Johnson, Year: 2018, "Synthesis, growth, optical, band gap energy and mechanical properties of semi organic nonlinear optical material: 2-Aminopyridine potassium dihydrogen orthophosphate lithium chloride (2APKDPL) crystal", Materials Science for Energy Technologies, Vol: 1, pp: 05-214.
2. A. Joseph Arul Pragasam; M. Divya; A. V. Pani Vignesh; G.Vinitha; P. Malliga, Year: 2018, "Analysis on linear and nonlinear optical properties of an efficient semi-organic crystal: Thiourea borate", Optics_& Laser_Technology_Vol: 107, pp: 428-434.
3. Vetrivel. S, et al, Year: 2013, "Effect of Zinc chloride on the growth and characterization of L proline cadmium chloride monohydrate semi organic NLO single crystal", Spectrochimica acta part A: Molecular and Biomolecular spectroscopy, Vol: 110, pp: 317-323.
4. Kandasamy, A, et al, Year: 2007, "Synthesis, growth and characterization of L proline cadmium chloride monohydrate crystals: A new nonlinear optical material", Crystal growth and design, Vol: 7, pp: 183-186.



Article Title: Investigation on the Impact of Thiourea on L-Proline Cadmium Chloride Single Crystal

5. Thomas Joseph Prakash, J; Kumararaman, S, Year: 2008, "Growth and characterization of L proline cadmium chloride monohydrate single crystals", Materials letters, vol: 62, pp: 4097-4099.
6. Santhakumari, R, et al, "Growth and characterization of thiosemicarbazide hydrochloride: A semi organic NLO material", Spectrochimica acta partA: Molecular and biomolecular spectroscopy, Vol: 82, pp: 102-107.
7. Nalini Jayanthi, S; Thamizharasan, K, Year: 2017, "Vickers microindentation hardness studies of DL methionine doped copper sulphate (MCS) single crystals", Materials today: proceedings, Vol. 4, pp: 358-362.
8. J. Beena, A. S; Jebamalar; S. Sindhusa; T. C. Sabari Girisun; A. Dhanusha, Year: 2021, "Optical limiting non-linear optical activity of hexaaqua copper (II) toluene-4-sulfonate for laser-driven optoelectronic application" J Mater Sci: Mater Electron.
9. Ushasree, P, M; Jayaval, R; Subramanian, C; Ramasamy, P; Year: 1997, Journal of Crystal growth, Vol.197, pp: 216-220.
10. Vetrivel, S, et al, 2013, "Effect of Zinc chloride on the growth and characterization of L proline cadmium chloride monohydrate semi organic NLO single crystal, Spectrochimica acta partA: Molecular and Biomolecular spectroscopy, Vol. 110, pp. 317-323.
11. Ubhashini, R; Arjunan, R; Year: 2018, "Synthesis and physiochemical properties of bis (L asparaginato) Zinc (II): A promising new nonlinear crystal with high laser damage threshold for short wavelength generation", Optics and laser technology, Vol. 101, pp. 248-256.
12. Nagapandiselvi, P; Baby, C, Gopalakrishnan, R, Year: 2015, "Synthesis, growth, structure and nonlinear optical properties of a semi organic 2-carboxy pyridinium dihydrogen phosphate single crystal", Optical materials.
13. Ollaa. M; Mailoud; Adly; H, Elsayed; H, Abu Fetouh, A; Abu ELazam, Year: 2018, "Synthesis and characterization of paramagnetic Isotropic Glycine Manganese chloride single crystal with various dopant concentrations", Results in Physics.
14. Suresh M, S; Asath Bahadur, S; Athimoolam, Year: 2016, "Synthesis, growth and characterization of a new hydrogen bonded organic tosylate crystal: L-alaninium p-toluenesulfonate for second order nonlinear optical applications", Journal of Materials Science: Materials in Electronics, Vol: 27, pp: 4578–4589.
15. Indumathi N; A. Hemalatha; E. Chinnasamy; A. Venkatesan; M.E. Raja Saravanan; K. Deepa; P. Matheswaran; S. Senthil; K. Kaviyarasu; R. Uthrakumar, Year: 2020, "Synthesis and characterization of L-threonine lithium chloride (LTLC)", A new semi-organic nonlinear optical single crystal for laser applications, Materials Today: Proceedings.