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### **Studies on the Growth, Optical, Thermal and Electronic Polarization Properties of Cadmium Chloride Doped L-Threonine (LTCC) NLO Crystals**

**C.Karnan<sup>1\*</sup>, A.R.Prabakaran<sup>2</sup> and K.Thamizharasan<sup>3</sup>**

<sup>1</sup>Department of Physics, Pachaiyappa's College, Chennai – 600030, India.

<sup>2</sup>Department of Physics, Sir Theagaraya College, Chennai – 600021, India., E-Mail:

[c.karnan@yahoo.com](mailto:c.karnan@yahoo.com)

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#### **ABSTRACT**

Single crystals of Cadmium Chloride doped L-Threonine (LTCC) were grown successfully by slow evaporation technique at room temperature using water as a solvent. Cadmium chloride as a dopant with 0.1-mole concentration was used. The grown crystals were characterized by X-ray diffraction, FTIR, UV-VIS spectral, microhardness and thermal techniques. The single crystal XRD analysis determines the cell volume and crystal system belongs to orthorhombic. The powder X-ray diffraction analysis was used to find out strain value, particle size, dislocation density and stacking fault. The presence of functional groups was confirmed by FTIR analysis. The energy gap was calculated using UV-VIS spectrum. TG-DTA analysis determines the thermal stability of the material and a sharp endothermic peak at 258°C shows good crystallinity of the grown crystal. The grown NLO crystal demonstrates its suitability for frequency conversion applications and second harmonic generation.

**KEYWORDS:** X-ray diffraction, Optical properties, Hardness and Electronic polarizability.

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#### **\*Corresponding Author:**

**C.Karnan**

Department of Physics,

Pachaiyappa's College,

Chennai 600 030, India.

Tel: +91 9600097511

E-Mail: [c.karnan@yahoo.com](mailto:c.karnan@yahoo.com)

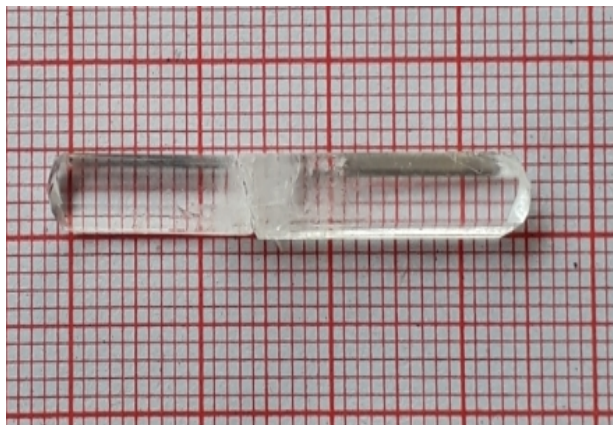
## **1. INTRODUCTION**

The organic nonlinear optical single crystals have widespread applications in the field of laser technology, light modulation, higher order harmonic generation, frequency conversion and memory storage<sup>1</sup>. In the recent years, there have been more and more researchers growing numerous nonlinear optical materials, because of their huge application in photonics, optoelectronic, laser remote sensing, optical switching, and frequency conversion, etc. Optically active amino acids show high efficiency in higher order harmonic generation and important material for coherent blue-green conversion and frequency doubling applications. Moreover, L-alanine, L-histidine, and L-threonine amino acids have wide transparency in the visible and UV ranges. Amino acid crystals have been proved to be suitable crystal for NLO applications because they are bipolar nature due to the presence of proton accepting  $-NH_2$  group and as well as proton donating  $-COOH$  group in them.

L-threonine is an important material in the amino acid family, which exhibits excellent second harmonic conversion efficiency greater than potassium dihydrogenphosphate. The growth and characterization of L-threonine based single crystals were reported earlier validated its importance as one of the applications-oriented optical material. In the present work, an attempt made to grow cadmium chloride doped L-threonine crystals by a slow evaporation technique. Structural, optical, thermal, mechanical, solid state parameters and SHG properties were discussed.

## **2. SYNTHESIS AND GROWTH**

The synthesis of cadmium chloride doped L-threonine was prepared by taking commercially available analytical reagent (AR) grade of L-threonine and cadmium chloride in 1:0.1 molar ratios were dissolved in deionized water and by repeated recrystallization process the material was used to prepare the saturated solution. The saturated solution was filtered using filter paper. The filtered solution was transferred to a petri dish within two days seed crystals were obtained. The obtained seeds were tied with thread and immersed in a saturated solution and allowed to evaporate at room temperature. Optically transparent single crystals of dimension  $36 \times 5 \times 3 \text{ mm}^3$  were harvested after 35 days. Fig.1 shows the photographs of as-grown crystal



**Fig.1. As-grown LTCC crystal**

### **3. RESULTS AND DISCUSSION**

#### **3.1.X-ray Diffraction Analysis.**

The single crystal X-ray diffraction studies were carried out on the good quality LTCC crystal using EnrafNonius CAD4-MV31 single crystal X-ray diffract meter with  $\text{MoK}\alpha$  ( $\lambda=0.71073\text{\AA}$ ) radiation at room temperature. The obtained data confirms that the LTCC crystal belongs to the orthorhombic crystal system and the unit cell parameters were found to be  $a=5.17\text{\AA}$ ,  $b=7.76\text{\AA}$  and  $c=13.65\text{\AA}$  and  $\alpha=\beta=\gamma=90^\circ$ . There is a slight variation in lattice parameter value of LTCC crystal compared to pure L-Threonine due to the incorporation of dopant<sup>10</sup>. The PXRD patterns recorded for cadmium chloride doped L-Threonine crystal using D8 Advance (Bruker) with  $\text{CuK}\alpha$  ( $\lambda=1.5406\text{\AA}$ ) radiation with a scanning range  $10^\circ$  to  $70^\circ$  and a scanning with a step size of  $1^\circ/\text{min}$  at room temperature. The obtained peaks for LTCC crystals were indexed and the pattern is shown in Fig.2. The presence of sharp peaks confirms the crystalline nature.

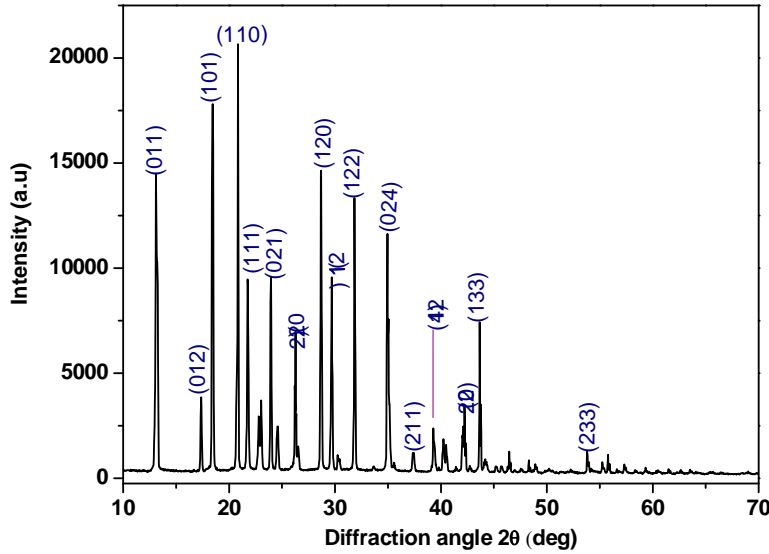


Fig.2 Powder XRD of LTCC crystal

### 3.2 Calculation of particle size, dislocation density, strain value, and stacking fault

The particle size (D) of the crystal is calculated using Debye Scherrer relation<sup>11</sup>

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad \text{-----(1)}$$

Where  $\lambda$  is the wavelength of the radiation used in powder XRD,  $\beta$  is the full width half maximum,  $\theta$  is the angle of diffraction. The strain value ( $\epsilon$ ) and dislocation density ( $\delta$ ) were calculated using relation:

$$\epsilon = \frac{\beta \cos\theta}{4} \quad \text{-----(2)}$$

$$\delta = \frac{1}{D^2} \quad \text{-----(3)}$$

where D is the particle size, the stacking fault ( $\alpha_{st}$ ) was calculated using the relation:

$$\alpha_{st} = \left( \frac{2\pi^2}{45(3\tan\theta)} \right) \beta \quad \text{-----(4)}$$

The calculated value of the particle size, strain value, dislocation density and stacking fault values are presented in table 1 and it shows that the crystals retain its orthorhombic system.

**Table1. Structural parameters of Cadmium chloride doped L-threonine**

FWHM	Particle size (D) Å	Dislocation density ( $\delta$ ) ( $\text{kg}/\text{m}^3$ ) $\times 10^{18}$	Strain value ( $\text{Lin}^{-2}$ $\text{m}^{-4}$ )	Stacking fault ( $\alpha_{st}$ )
0.176	8.13354	1.51161	0.04451	0.16837
0.181	7.89710	1.60348	0.04466	0.16288
0.185	7.69841	1.68732	0.04548	0.14702
0.190	7.42173	1.81546	0.04625	0.11895
0.228	6.05712	2.72563	0.05436	0.10572

### 3.3.FTIR Analysis

The presence of functional groups in the sample was recorded using a Perkin-Elmer spectrometer at room temperature in the wavenumber range of 450-4000 $\text{cm}^{-1}$ . The observed peak at 489 $\text{cm}^{-1}$  is assigned due to the torsion mode of  $\text{NH}_3$ . The sharp peak observed 540 $\text{cm}^{-1}$  is due to C-C-N group deformation vibration. The peak found at 772 $\text{cm}^{-1}$  is due to torsion mode of  $\text{COO}^{12}$ . The stretching of the CN structure is related to the sharp peak observed at 1014 $\text{cm}^{-1}$ . The band between 1112 and 1235 $\text{cm}^{-1}$  is due to the rocking of the  $\text{NH}_3^+$  structure. The bending vibrations of CH group of LTCC are found at 1305 $\text{cm}^{-19,13}$ . The peak at 1412 $\text{cm}^{-1}$  is due to  $\text{CO}_2^-$  symmetric stretching vibration. Strong  $\text{NH}_3^+$  deformation band observed at 1515 $\text{cm}^{-1}$ . Weak  $\text{NH}_3^+$  deformation band observed at 1618 $\text{cm}^{-1}$ . The weak band due to symmetric stretching vibrations of  $\text{NH}_3^+$  is observed at 2601 $\text{cm}^{-1}$ . The band due to asymmetric stretching of  $\text{NH}_3^+$  is assigned at 3085 $\text{cm}^{-14,15}$ . The FTIR assignments confirm the presence of an amino acid functional group of the grown crystal.

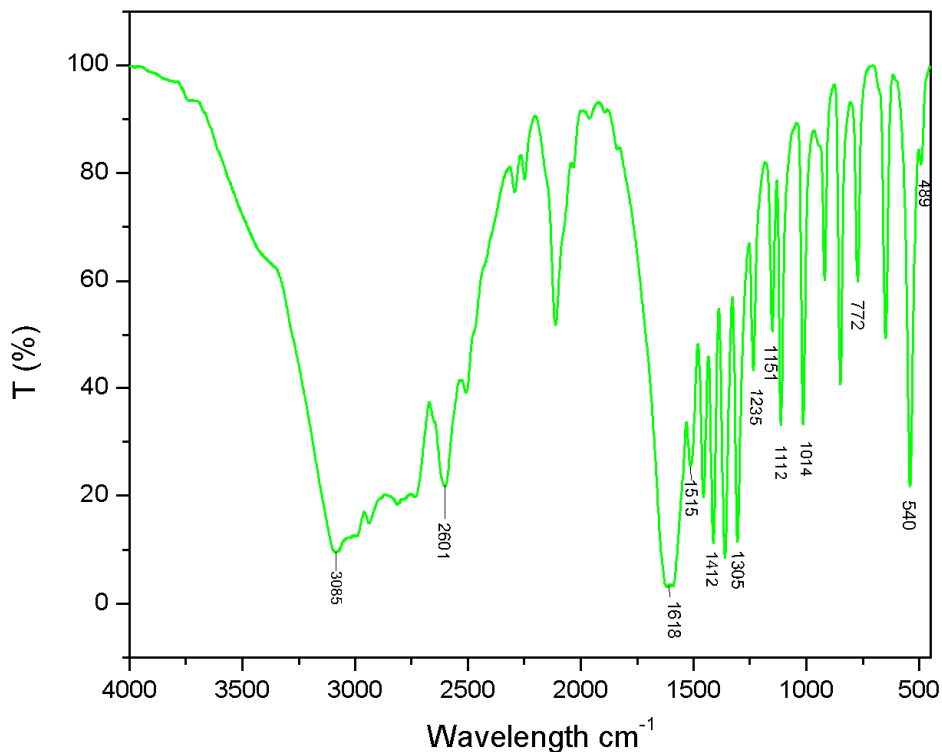


Fig.3 FTIR spectrum of LTCC crystal

### 3.4. UV-Visible spectra

The optical transmission spectrum of cadmium chloride doped L-threonine crystals was shown in Fig.4.a. The UV transmission studies were carried out using Perkin Elmer LAMDA 950 with range 200-900nm using LTCC crystals. Fig.4.a shows that the material has low absorption and high transmission in the entire visible region which are essential properties of amino acids. The lower  $\lambda_{cut}$ (nm) of LTCC was found to be 233 nm which shows that the material is suitable for NLO activity. The measured transmission (T) was used to calculate the absorption coefficient ( $\alpha$ ) using relation<sup>16</sup>.

$$\alpha = \frac{1}{d} \log \left( \frac{1}{T} \right) \quad \text{----- (5)}$$

Where  $d$  is a thickness of the crystal and  $T$  is the transmission. The optical energy gap can be measured using the expression<sup>17</sup>.

$$(\alpha h\nu)^2 = A(E_g - h\nu) \quad \text{----- (6)}$$

Where  $A$  is a constant,  $\nu$  is the frequency of incident radiation,  $h$  Planck's constant and  $E_g$  energy gap. Fig.4.b plotted between the energy gap and  $(h\nu)$  with the product of the absorption coefficient and the energy gap at an optimum condition for the direct allowed transition. The

measured energy gap of LTCC crystal was 5.1eV. The energy gap is calculated theoretically using formula,

$$Eg = \frac{1238.23}{\lambda} eV \quad \text{-----(7)}$$

where lower cut-off wavelength  $\lambda_{cut}$  were substituted in equation (2) the energy gap of LTCC was found to be 5.31eV, the obtained value is in good agreement with tauc's plot. The amount of absorption is explained by extinction coefficient (K) by propagating electromagnetic wave through a medium and it can be determined using the relation<sup>18</sup>.

$$K = \frac{\alpha\lambda}{4\pi} \quad \text{-----(8)}$$

The reflectance (R) and refractive index (n) are calculated using the following relation<sup>19,20</sup>.

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t) + \exp(\alpha T)}}{1 + \exp(-\alpha t)} \quad \text{----- (9)}$$

$$n = \frac{-(R+1) \pm \sqrt{(1-3R^2+10R-3)}}{2(R-1)} \quad \text{----- (10)}$$

The refractive index (n) of LTCC crystals were determined by reflectance (R) using the relation (9, 10). The refractive index of LTCC crystals was found in the visible region (n=1.4) at the wavelength of 233 nm. Hence LTCC crystals are suitable for NLO applications and optoelectronics devices fabrications.

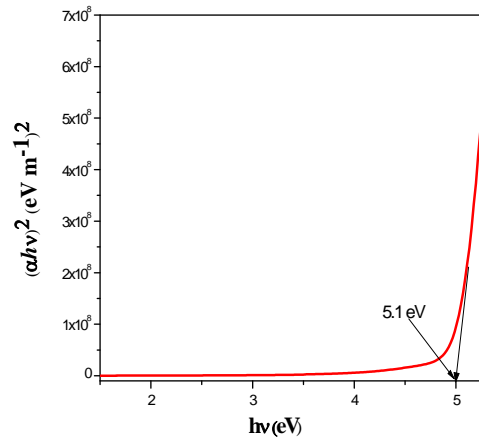
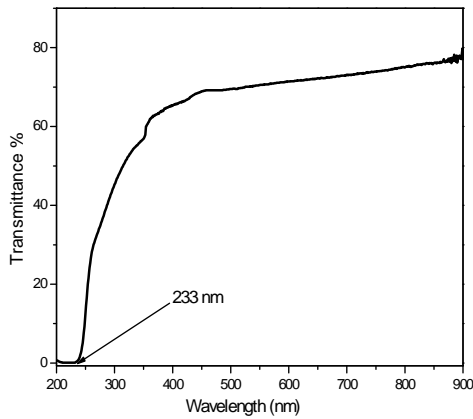


Fig.4.a) Optical transmission spectrum of LTCC crystal      Fig.4.b) Photon energy vs  $(\alpha hv)^2$  for LTCC crystal

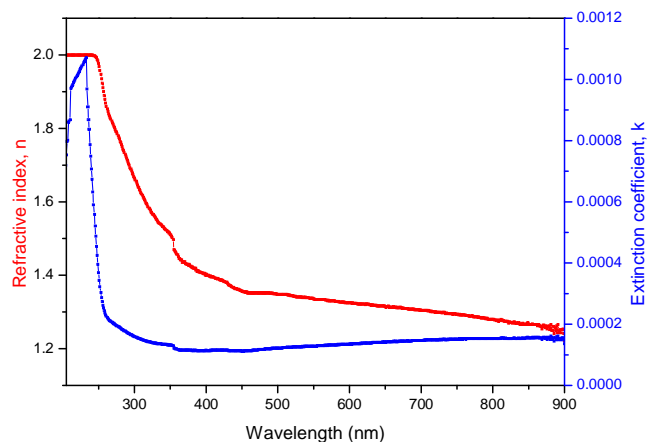


Fig.4.c) Variation of the refractive index and extinction coefficient vs wavelength of the LTCC crystal

### 3.5. TG-DTA analysis

Thermodynamic properties of LTCC crystals were analyzed using thermo-gravimetric (TG) and differential thermal analysis (DTA) was carried for understanding the essential behaviour of the material under the heating rate of 10K/min using NETZSCH STA 499 F3 Jupiter in a nitrogen atmosphere. TG and DTA were recorded in the range of 25°C – 550°C is shown in fig.5. The LTCC sample was taken weighing 4.74mg for measurement. The TG curve shows maximum weight loss starting at around 241°C and ending at 264°C. The DTA trace clearly shows the melting point of LTCC is at 258°C through its sharp endothermic peak. The decomposition in the TG trace is coinciding with the endothermic peak of the DTA trace. The TG-DTA analysis confirms that the material is thermally stable up to 241°C which can be used for NLO applications up to this temperature. The final residue weight left was about 2.82% after heating above 545°C.



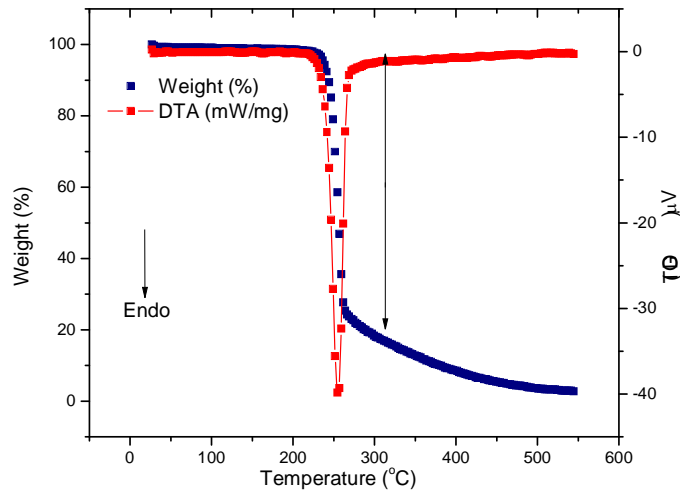


Fig.5. TG-DTA spectrum of LTCC crystal.

### 3.6. Microhardness studies

The mechanical strength of the crystal, molecular bindings, yield strength and elastic constant of the material can be determined using Vicker’s diamond pyramidal indenter. In the field of device fabrication, the mechanical strength of a crystal plays a major role<sup>21</sup>. A good quality crystal was taken and placed on the Vickers microhardness tester and different loads have been applied in a time interval of 10s. The Vickers hardness number  $H_v$  was calculated using the relation

$$H_v = \frac{1.854P}{d^2} (\text{kg/mm}^2) \text{ ----- (11)}$$

where  $p$  is the applied load (kg),  $d$  is the diagonal length (mm) and geometrical factor for the diamond pyramid is 1.8544 is a constant. Fig.6. a) shows that an increase in load increases the hardness number with the load up to 200g. This indicates that the crystal has the reflection of a reverse indentation size effect (RISE). The Mayer’s index ( $n$ ) can be calculated using Mayer’s relation between  $p$  load and  $d$  diagonal length<sup>22</sup>.

$$P = A d^n \text{ -----(12)}$$

Where the exponent ( $n$ ) is work hardening coefficient. Fig.6.b shows fitting straight line plot between  $\log P$  and  $\log d$ . The Mayer’s index number  $n$  was found to be 2.42 from the slope. According to Onitsch<sup>23</sup> for hard crystal  $n$  value lies between 1 and 1.6, for soft crystals more than 1.6. From the hardness study grown LTCC crystal belongs soft crystal category. The doping of cadmium chloride to the L-threonine crystal enhances the strength of bonding in the host material and increases the hardness number.

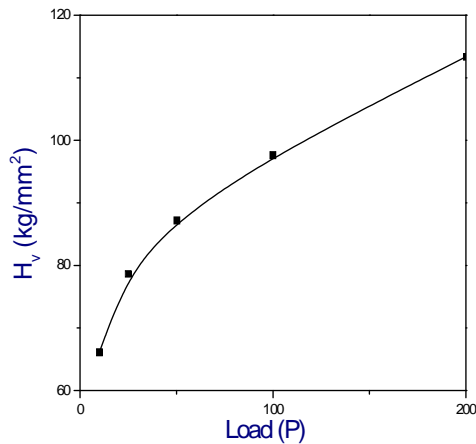


Fig.6. a) Vicker's microhardness of LTCC crystal

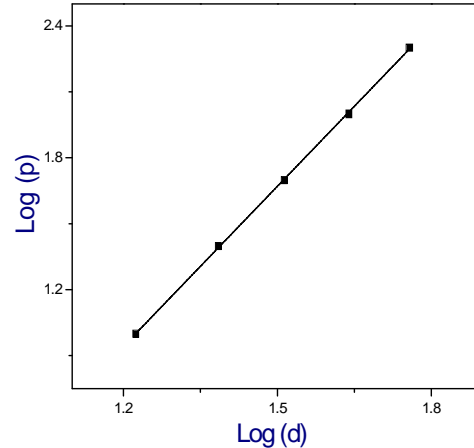


Fig.6. b) plot of Log P vs Log d

### 3.7 Electronic polarization

Solid state parameters are essential for the advisable efficiency of nonlinear effect and important in the electro-optic polarization of the material. It is evident from the theoretical calculations shows the dielectric constant at high frequency is fully dependent on the valence electron plasma energy, Fermi energy, Penn gap and electronic polarizability<sup>24</sup>. The valence electron plasma energy  $\hbar\omega_p$  is determined using the following relation<sup>25</sup>

$$\hbar\omega_p = 28.8 \left( \frac{z\rho}{M} \right)^{1/2} \text{-----(13)}$$

where M is the molecular weight of the LTCC crystal, Z is the total number of a valence electron,  $\rho$  is the density of the material,  $\hbar = h/2\pi$  and  $\omega_p$  is plasma angular frequency. The Penn gap energy is calculated using the following relation<sup>26</sup>

$$E_p = \frac{\hbar\omega_p}{\sqrt{(\epsilon_\infty - 1)}} \text{-----(14)}$$

Where  $\epsilon_\infty$  is the dielectric permittivity. The Fermi energy is given by:

$$E_F = 0.2948 (\hbar\omega_p)^{4/3} \text{-----(15)}$$

The electric polarizability ( $\alpha$ ) of the LTCC crystal was determined using the relation<sup>27</sup>

$$\alpha = \left[ \frac{(\hbar\omega_p)^2 S_o}{(\hbar\omega_p)^2 S_o + 3E_p^2} \right] X \frac{M}{\rho} 0.0396 X 10^{-24} \text{cm}^3 \text{-----(16)}$$

Where  $S_o$  is a constant for material which is given by:

$$S_o = 1 - \left[ \frac{E_p}{4E_F} \right] + \frac{1}{3} \left[ \frac{E_p}{4E_F} \right]^2 \text{-----(17)}$$

The value of electronic polarizability ( $\alpha$ ) is also estimated by using Clausius-Mossotti relation, the ( $\alpha$ ) value obtained at equation (16) and (18) are in good agreement

$$\alpha = \frac{3M}{4\pi N_a \rho} \left( \frac{\epsilon_{\infty} + 1}{\epsilon_{\infty} + 1} \right) \text{-----(18)}$$

Where  $N_a$  is Avogadro number using optical band gap the value of electronic polarizability ( $\alpha$ ) can also be obtained, which is given by,

$$\alpha = \left[ 1 - \frac{\sqrt{E_g}}{4.06} \right] X \frac{M}{P} X 0.396 X 10^{-24} cm^3 \text{-----(19)}$$

Where  $E_g$  is the optical band gap of the material. The calculated parameters for the LTCC crystals are given in table.2

**Table 2. Solid state parameters of cadmium chloride doped L-threonine**

Parameters	Value
Plasma energy ( $\hbar\omega_p$ )	20.94 (eV)
Penn gap ( $E_p$ )	2.59 (eV)
Fermi energy ( $E_f$ )	17.02 (eV)
Electronic polarizability (Penn analysis)	$3.42 \times 10^{-23} cm^3$
Electronic polarizability (Clausius-Mossoti)	$3.44 \times 10^{-23} cm^3$
Electronic polarizability (optical band gap)	$2.97 \times 10^{-23} cm^3$

### 3.8 Kurtz-Perry Powder Second Harmonic Generation Studies

The grown crystals of cadmium chloride doped L-threonine crystals were subjected to Kurtz-Perry<sup>28</sup> powder second harmonic generation (SHG) test to confirm the nonlinear optical (NLO) property. The crystals were taken in a powder form and tightly packed between glass slides. Nd:YAG Q-switched laser beam of wavelength 1064 nm was made to fall on the powder sample. The emission of green light from the sample confirms the second harmonic generation in the crystal. The powder sample of potassium dihydrogen phosphate crystals was used as a reference material in the SHG measurement. The efficiency of LTCC crystals was found to be 1.3 times greater than that of the KDP crystals.

### 4. CONCLUSION

Optically good transparent cadmium chloride doped L-threonine crystals were grown by a slow evaporation technique. Single crystal X-ray diffraction and powder X-ray diffraction confirms that the crystal has good crystalline nature and it belongs to the orthorhombic crystal system. Presence of expected functional groups was confirmed by the FTIR spectrum. From the UV transmission spectrum, energy gap and cut-off wavelength were found to be 5.1 eV and 233 nm. TG-DTA curve shows the melting point of the crystal 258° C. From the hardness study grown LTCC crystal belongs soft crystal category. Various solid state parameter values such as plasma energy, Penn gap  $E_p$ , Fermi energy  $E_f$  and electronic polarizability were determined for the grown LTCC crystal. SHG efficiency confirms that the crystal has greater efficiency than KDP. The studies carried

out on title material conclude that transparency of the material is enhanced due to doping and mechanical strength is increased. This material has great potential for nonlinear optical devices fabrication.

### **Compliance with Ethical Standards:**

#### ***Funding:***

There is no funding involved with the current study.

#### ***Conflict of Interest:***

The authors declare that they have no conflict of interest.

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