

Investigation on Growth and Optical Properties of LVCC Single Crystals

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Abstract

L-valine cadmium chloride (LVCC) single crystals were grown by slow evaporation technique with different concentrations (0.25, 0.5, 0.75 and 1.0 mole) of CdCl₂. All the grown crystals were subjected to single crystal X-ray diffraction analysis. Solid state parameters were calculated for the grown crystals. The optical properties of the crystals were investigated by UV-Vis. absorption spectroscopy. The results revealed that, the wider bandgap and large transparency in the visible region along with higher polarizability of the grown crystals are highly useful in optoelectronic devices. Also according to our needs, one can tune the optical and electrical properties of LVCC crystals by adjusting the concentration of CdCl₂ in LVCC.

I. Introduction

From last few decades the search of new materials from organic, inorganic and semiorganic class and their crystal growth with unique nonlinear optical properties is in progress. Currently the use of optical single crystals has been increased due to their wide application in the field of photonics such as high-speed information processing [1], frequency conversion [2], optical communication [3], high optical disk data storage [4] etc. A great deal of effort was put in the development of nonlinear optical (NLO) materials for second harmonic generation (SHG). Second-harmonic generation (SHG) in nonlinear optical crystals is one of efficient and widespread methods of laser frequency conversion into other frequency ranges. The inherent limitations on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device grade organic single crystals have made scientists adopt newer strategies. The obvious one was to develop hybrid inorganic-organic materials with little trade-off in their respective advantages.

The second order optical effect is concerned in both inorganic and organic materials. In this concern, the inorganic materials show the good mechanical and thermal stability with high transparency range limiting their second order coefficient. The organic compounds with electron rich (donor) and deficient (acceptor) substituents provide an asymmetric charge distribution in the π electron system and show large nonlinear optical response. This new class of materials has come to be known as the metal organics [5]. Crystals of amino acid salts (amino acids with inorganic salts) are found to be promising second order nonlinear optical materials. Amino acids are interesting materials for NLO application as they

contain proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH₂) group. Especially some amino acids like arginine [6], lysine [7], L-alanine [8] and γ -glycine [9] are evidently showing NLO activity because they have a donor NH₂ group and acceptor COOH group with a possibility of charge transfer. The organic crystals exhibit higher second order nonlinear coefficient, but poor in thermal and mechanical behavior and it may not be suitable for many device applications [10]. To overcome this difficulty, optically active amino acids of crystalline solids are combined with inorganic host favorable for good thermal and mechanical properties with high nonlinear optical coefficient like L-alanine potassium chloride [11], L-alanine cadmium chloride [12] and L-proline potassium chloride [13] are already reported.

Among the various amino acids, L-valine (C₅H₁₁O₂N) is the third simplest of the aliphatic amino acids, crystallizing in two forms: *gauche* and *trans* [14]. It has aliphatic non-polar side chain and has both a primary amino group and a primary carboxyl group. The carboxylate acid group donates its proton to the amino group. So in solid state, amino acid exists as zwitterions, which create hydrogen bonds, in the form of N-H⁺ -O-C, which are very strong bonds. Hydrogen bonds have also been used in the possible generation of noncentrosymmetric structures, which is a prerequisite for an effective SHG crystal [15]. The importance is that amino acids contain chiral carbon atom and crystallize in the noncentrosymmetric space groups, therefore, they are potential candidates for optical second harmonic generation. With the aim of finding new crystal with better NLO efficiency, in our present investigation on semiorganic crystal of L-valine cadmium chloride

(LVCC) with different concentration of CdCl_2 i.e. $\text{LV}(\text{CC})_{0.25}$ (for 0.25 mole CdCl_2), $\text{LV}(\text{CC})_{0.50}$ (for 0.50 mole CdCl_2), $\text{LV}(\text{CC})_{0.75}$ (for 0.75 mole CdCl_2) and LVCC (1 mole CdCl_2) is grown successfully for the first time from aqueous solution by the slow evaporation method. All the grown crystals were subjected to characterize structurally and optically.

II. Experimental

2.1. Synthesis and Growth of LVCC

Analytical reagent (AR) grade samples of L-valine and cadmium chloride (CdCl_2) were obtained from Merck India Ltd. Double distilled water was used as the solvent for the growth of L-valine cadmium chloride (LVCC) single crystals.



The purity of the salt was improved by repeated recrystallization process in double distilled water at least three times and was used for crystal growth.

The solubility of pure LV and various concentrations (0.25, 0.50, 0.75 and 1.0) of CdCl_2 in LVCC salts in double distilled water were found for six different temperatures (25, 30, 35, 40, 45 and 50 °C). By using the solubility data, the above synthesized salt was used for recrystallization process. Supersaturated solution of 100 ml was prepared from solubility curve at 40 °C using recrystallized LVCC salt and was filtered with microfilters and taken in a glass beaker of 100 ml capacity. Then the beaker was sealed with perforated plastic paper and placed at constant temperature bath

LVCC was synthesized by reaction between L-valine ($\text{C}_5\text{H}_{11}\text{NO}_2$) and cadmium chloride (CdCl_2) purchased from Merck India Ltd. They were taken in the different molar ratio (1:0.0 (pure L-valine), 1:0.25 ($\text{LV}(\text{CC})_{0.25}$), 1:0.50 ($\text{LV}(\text{CC})_{0.50}$), 1:0.75 ($\text{LV}(\text{CC})_{0.75}$) and 1:1 (LVCC)). The calculated amount of reactants was dissolved in double distilled water and the solution was continuously stirred for an hour maintaining the temperature of 40 °C. After the condition of saturation was achieved, 0.1N HCl was added with the above solution to adjust the pH ~4.5 to 5. The chemical reaction takes place to form the precipitate of L-valine cadmium chloride salt. LVCC was formed according to the following addition reaction:

and the temperature of the bath was maintained as 30 °C. LVCC crystals were harvested in a growth period of 20 to 25 days by slow evaporation of the solvent.

The temperature dependent solubility of pure LV and various concentration of CdCl_2 in LV crystals are shown in Figure 1. It is found that the solubility of pure LV, 0.25 mole CdCl_2 mixed LV ($\text{LVCC}_{0.25}$), 0.50 mole CdCl_2 mixed LV ($\text{LVCC}_{0.50}$), 0.75 mole CdCl_2 mixed LV ($\text{LVCC}_{0.75}$) and 1 mole CdCl_2 mixed LV (LVCC) crystals increases with increase of temperature. Solubility of LVCC crystals increases with increasing concentration (0.25 to 1.0 mole in steps of 0.25) of CdCl_2 in LVCC crystals.

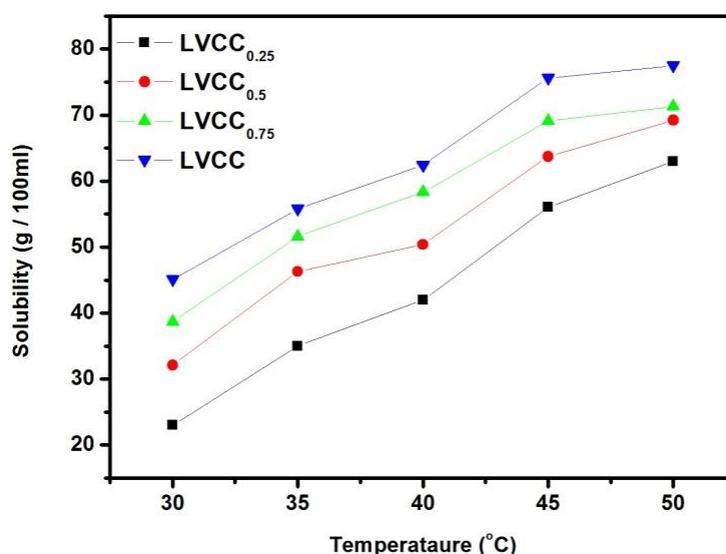


Figure 1: Solubility curve of LVCC crystal with different concentrations of CdCl_2

2.2. Characterization

The single crystal X-ray diffraction studies of the grown crystals were carried out using Bruker Nonius APEX II - V2.D2 single crystal X-ray diffractometer with MoK_α ($\lambda = 0.717 \text{ \AA}$) radiation. The optical

absorption spectrum was recorded in the range of 190-800 nm, using Jasco V - 630. The solid state parameters such as valence electron plasma energy ($\hbar\omega_p$), Fermi energy (E_F), Penn gap energy (E_p) and electronic polarizability (α) is calculated using the following relations [17],

$$\hbar\omega_p = 28.8 \left(\frac{Z\rho}{M} \right)^{1/2} \quad (1)$$

$$E_p = \frac{\hbar\omega_p}{(\epsilon_\infty - 1)^{1/2}} \quad (2)$$

$$E_F = 0.2948 (\hbar\omega_p)^{4/3} \quad (3)$$

The electronic polarizability (α) of the grown crystals were calculated using a relation,

$$\alpha = \left(\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + E_p^2} \right) \left(\frac{M}{\rho} \right) 0.396 \times 10^{-24} \text{ F m}^2 \quad (4)$$

where S_0 is a constant given by

$$S_0 = 1 - \left(\frac{E_p}{4E_F} \right) + \frac{1}{3} \left(\frac{E_p}{4E_F} \right)^2 \quad (5)$$

The value of α obtained from the above equation closely matches with that obtained from Clausius-Mossotti relation,

$$\alpha = \frac{3}{4} \frac{M}{\pi N_a \rho} \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right) \quad (6)$$

The NLO test of LVCC crystals were evaluated by the Kurtz and Perry powder technique [16] using a Q-switched, mode locked Nd:YAG laser emitting 1.06 μm , 8 ns laser pulses with spot radius of 1 mm.

III. Results and Discussions

3.1 Structural Analysis

The single crystals were subjected to single crystal X-ray diffractometer with M_oK_α radiation of wavelength $\lambda = 0.717 \text{ \AA}$ is to determine the unit cell parameters and space group. The observed structural data for all the crystals considered in the present study are presented in Table 1. From this table it is observed that the different concentration of CdCl_2 admixed LVCC crystallize in monoclinic system with space group $P2_1$. This implies that all the crystal systems are noncentrosymmetric which is the primary requirement for a material to be second order nonlinear. The lattice parameters of 0.25 mole CdCl_2 mixed LVCC, 0.50 mole CdCl_2 mixed LVCC, 0.75 mole CdCl_2 mixed LVCC and 1 mole CdCl_2 mixed LVCC were found to be different from pure LV [17]. As the incorporation of CdCl_2 in L-valine lattice, there is no systematic variation in lattice parameters of LVCC crystals with respect to increasing concentration of CdCl_2 from 0.25 mole to 1 mole. However, the overall unit cell volume expansion take place when we increase the concentration of CdCl_2 in LVCC lattice. This reveals that the increasing concentration of CdCl_2 in LVCC reconstructs the lattices in all the three dimensions without affecting the parent crystal lattice (L-valine) structure.

Table 1: Single crystal XRD data of LVCC with different concentrations of CdCl₂

DATA	L-valine [17]	LV(CC) _{0.25}	LV(CC) _{0.50}	LV(CC) _{0.75}	LVCC
a (Å)	9.701	9.8633	9.9732	10.1379	10.2841
b (Å)	5.261	5.2976	5.2285	5.4016	5.6214
c (Å)	11.953	12.1397	13.0241	12.6612	12.5457
V(Å ³)	610.004	634.079	677.886	692.804	721.610
α (°)	90	90	90	90	90
β (°)	90.66	91.583	93.483	92.250	95.766
γ (°)	90	90	90	90	90
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁	P2 ₁	P2 ₁	P2 ₁	P2 ₁

3.2 UV-Vis. Analysis

The optical absorption spectrum of LVCC with different concentration of CdCl₂ in the wavelength range from 190 - 800 nm is shown in figure 2. The spectra showed that for all the four concentrations of CdCl₂, the crystals have complete transparency in the visible region. A good optical transmittance is desirable property of an NLO crystal since the absorption, if any, in an NLO material near the fundamental or the second harmonic will lead to the loss of conversion efficiency in those wavelengths. Wider the transparency window more will be the practical applicability of that material. Pure L-valine crystal has UV cut off 240 nm [17]. From figure, it is found that the shape and position of the absorption peaks of CdCl₂ mixed LVCC has some significant blue shift from the pure LV except LVCC_{0.75}. As it is clear from Figure 2, the concentration (from 0.25 to 1 mole) of CdCl₂ in LVCC has not affect the optical absorbance in the entire visible range, however there is a small significant variation in UV range.

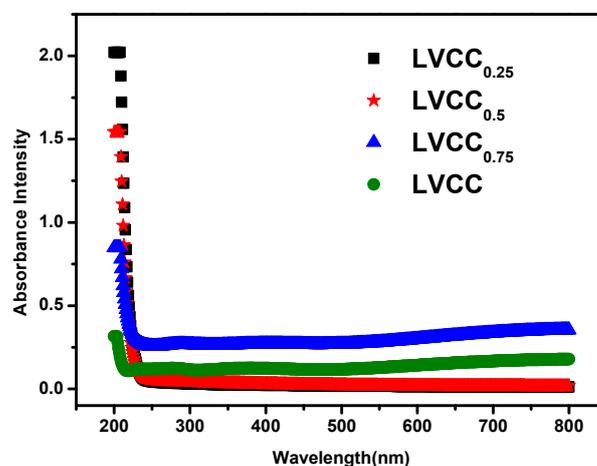


Figure 2: Optical Absorption Spectra of LVCC single crystals with different concentration of CdCl₂

The Plot of optical bandgap determination from UV-Vis absorption data of different concentration of CdCl₂ mixed LVCC single crystals are shown in Figure 3. The absorption coefficient α can be determined using the relation,

$$\alpha = \frac{2.303 \log (\text{absorption})}{\text{Thickness of the sample}} \quad (7)$$

The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) can be written as [18]: $(\alpha h\nu) = A (h\nu - E_g)^n$, (8)

where, A is a constant, E_g is the bandgap energy of the material and exponent n depends on the type of transition [18]. The value of optical bandgap is calculated by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs $h\nu$ graph to $h\nu$ axis.

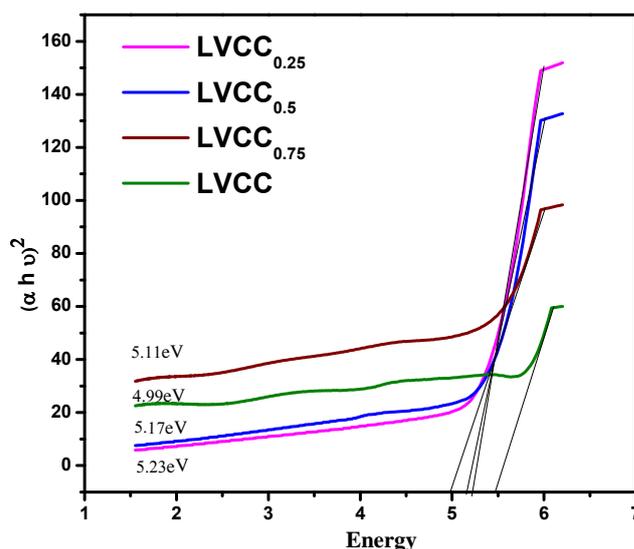


Figure 3: Tau plot for LVCC single crystals with different concentration of CdCl₂

The band gap of pure L-valine single crystal is 3.75eV [17]. From the Figure 3, it is evident that the UV cutoff wavelength of CdCl₂ mixed LVCC crystal decreases with increasing concentration of CdCl₂ in LVCC except for LVCC_{0.75} crystals. It reveals that the UV cutoff wavelength of LVCC crystals can be tuned by adjusting the concentration of CdCl₂ in LVCC which makes it suitable for fabricating optoelectronic devices as per our needs. A UV cut-off below 300 nm is sufficiently low for SHG laser radiation at 1064 nm or other applications in the blue region. The absence of absorption bands in the visible region and the wide bandgap of the grown crystal attest to the suitability of the grown crystal for photonic and optical applications [19]. All the grown crystals have larger bandgap than the pure LV single crystals. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [20].

The extinction co-efficient (k) of the grown crystals were plotted against the wavelength given in Figure 4. It suggests that for all the wavelengths k increases linearly for all the concentrations of CdCl₂. Extinction coefficient" is the imaginary part of the complex index of refraction, which also relates to light absorption.

$$K = \frac{\alpha \lambda}{4\pi}$$

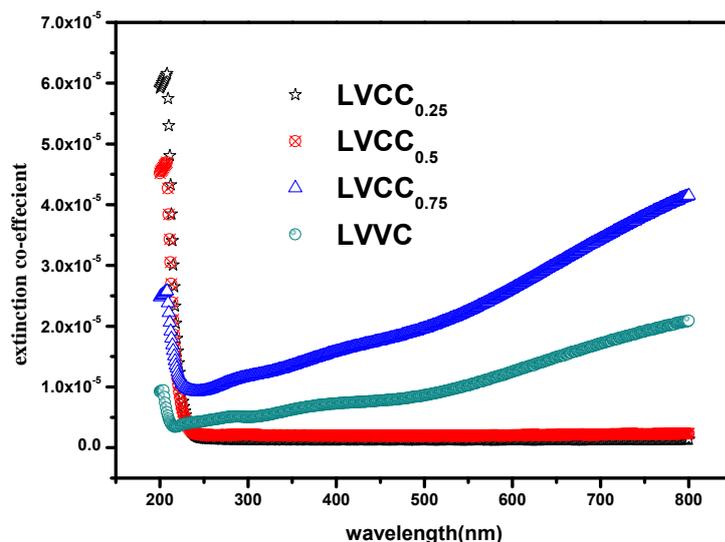


Figure 4 : Variation of Extinction coefficient of LVCC single crystals with different concentrations of CdCl₂

3.3 Solid state Parameters Analysis

Solid state parameters are necessary to analyze second harmonic generation efficiency of the grown crystals. The value of valance electron Plasma energy (E_p), Penn gap energy, Fermi energy (E_F) and polarizability (α) of the grown crystals were calculated by the formulas given by Vasdevan et al. [21]. The calculated values are given in Table 2. The values of molecular polarizability were compared with the values obtained by Clausius-Mosotti equation [17]. These values are compared with those of standard material KDP. From the table, it is clear that, the solid state parameters are found to be higher than those of KDP. In particular, the polarisability of all the grown crystals were nearly greater than 2.5 orders that of KDP which intern conforms that, all the grown crystals have almost same orders of SHG efficiency than that of KDP.

Second harmonic generation of the grown crystal was confirmed using Kurtz and Perry powder technique [16]. A high intense beam of laser wavelength 1064nm was allowed to illuminate the sample with pulse width of 8 ns. The emission of green radiation 532nm from the sample confirms that the material exhibits nonlinear optical property. The output radiation from the crystal was allowed to fall on a photomultiplier tube which converts the light signal into electrical signal. The second harmonic generation is confirmed by the emission of green light and its efficiency is found to be higher than that of KDP.

Table 2: Calculated solid state parameters for LVCC single crystals with different concentrations of CdCl₂

Solid state parameter	LV [17]	LV(CC) _{0.25}	LV(CC) _{0.50}	LV(CC) _{0.75}	LVCC	KDP [17]
Plasma energy (eV)	15.02	22.008	19.612	17.930	16.612	17.33
Penn gap (eV)	1.42	2.162	1.966	1.836	1.730	2.39
Fermi energy (eV)	10.83	17.996	15.438	13.702	12.379	12.02
Polarizability ($\times 10^{-23}$)	4.481	4.33	5.45	6.51	7.57	2.14
Polarizability from Clausius-Mosotti ($\times 10^{-23}$)	4.931	4.22	5.31	6.34	7.38	2.18
SHG theoretical	2.09	2.02	2.546	3.042	3.530	1
Experimental	-	1.313	1.668	2.068	2.578	1

IV. Conclusion

Single crystals of LVCC with different concentrations of CdCl₂ were grown by solution technique. Single crystal XRD data revealed that grown crystals crystallize in monoclinic structure. The absence of absorption bands in the visible region and the wide bandgap of the grown crystal attest to the suitability for photonic and optical applications. Also solid-state parameter calculation proved that mixing of L-valine with equimolar concentration of CdCl₂ highly enhances the nonlinear optical parameters. The theoretical values agreed well with that of measured SHG values. High Polarizability values of the grown crystals predict the applications of grown crystals in photonic industry than the pure L-valine crystals.

References

- [1.] M. Victor Antony Raj and J. Madhavan, Archives of Physics Research, 2 (1) (2011) 160-168.
- [2.] B.G.Penn,B.H.Cardelino,C.E.Moore,A.W.S hields,D.O.Frazier,Prog.Cryst.Growth Charact. 22(1991)19–51.
- [3.] N.P.Zaitseva, L.Carman,Prog.Cryst.GrowthCharact.43 (2001)1–118.
- [4.] J.Badan, R.Hierle, A.Perigaud, J.Zyss,in: D.J.Williams (Ed.), NLO properties of Organic Molecules and Polymeric Materials .American Chemical Symposium Series 233,AmericanChemicalSociety,Washington, DC,(1993).
- [5.] Mohd. Shkir , S.Alfaify , M.AjmalKhan , ErnestoDieguez , Josefina Perles, Journal of Crystal Growth 391(2014)104–110.
- [6.] U. Karunanithi, S. Arulmozhi and J. Madhavan, Journal of Applied Physics (IOSRJAP) 1(2) (2012), 14-18.
- [7.] V Vasudevan, R Ramesh Babu, A Reicher Nelcy, G Bhagavannarayana And K Ramamurthi, Bull. Mater. Sci., 34(3) (2011) 469–475.
- [8.] P. Malliga and A. Joseph Arul Pragasam, Journal of Russian Laser Research 34(4) (2013) 346-350.
- [9.] A. Ruby, S. Alfred Cecil Raj, International Journal of Chem Tech Research .5(1)(2013) 482-490.
- [10.] V. Azeeza, A. Joseph Arul Pragasam, T.G. Sunitha, Photonics Letters Of Poland, 6 (3), (2014) 105-107.
- [11.] D.Prabha and S.Palaniswamy, Rasiyan J.Chem, 3(3) (2010), 517-524.
- [12.] S. Vinu, A.C. Sajikumar, Scientia Acta Xaveriana, 4(1) (2013), 111-116.
- [13.] S. Vetrivel, R. Rajasekaran, Advanced Materials Research 584(2012), 60-64.
- [14.] Torii K, Iitaka Y. Acta Cryst, B26: (1970) 1317.
- [15.] S. Suresh and D. Arivuoli, Journal of Minerals & Materials Characterization & Engineering, 10(12)(2011).1131-1139.
- [16.] S.K. Kurtz, and T.T. Perry, J.Appl. Phys.39 (1968) 3798
- [17.] S.Suresh, A.Ramanand, D.Jayaraman, P.Mani and K. Anand, International Journal of ChemTech Research ,3(1)(2011), 122-125.
- [18.] A. K. Chawla, D. Kaur, and R. Chandra, Opt. Mater. 29(8) (2007) 995-998 .
- [19.] Deepa Jananakumar, P Mani, International Journal of ChemTech Research 5(1)(2013), 113-120.
- [20.] D. D. O Eya, A. J. Ekpunobi, and C. E. Okeke, Acad. Open Internet J. (2006) 17.
- [21.] P. Vasudevan,S. Sankar,and D. Jayaraman, Bull. Korean Chem. Soc. 34(1)2013,128-132.