Studies on the Synthesis, Spectral, Optical and Thermal properties of Zinc chloride doped L-Valine cadmium chloride crystals

[1]R.Sajitha, [2] Dr.S.Dawn Dharma Roy
[1]Research scholar, [2]Assistant Professor
Nesamony memorial christian college Marthandam, Affiliated to Manonmaniam Sundaranar University Tirunelveli.
Department of Physics, Faculty of Science,

Abstract - A new semi organic non- linear optical material, L-valine cadmium chloride (LVCC crystal) doped with Zinc chloride has been grown successfully by slow evaporation technique. The grown crystal was characterized by using powder X- ray analysis and confirmed the crystalline nature of the title compound. The presence of functional groups of the grown crystal has been confirmed by Fourier Transform Infrared Spectroscopy (FTIR) analysis. TGA/DTA studies revealed the thermal stability of grown crystals. The optical absorption study was examined by UV-VIS spectrum. The suitability of NLO application of this material was studied by optical absorption studies and second harmonic generation efficiency by Kurtz Powder method.

Keywords **- Slow evaporation method, XRD, FTIR, UV spectrum, Thermal studies.**

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1. INTRODUCTION

Growth of Non Linear Optical (NLO) single crystals with good quality initiates the development of many novel devices in the field of optoelectronics and optical communication such as optical modulator, optical data storage and optical switches [1-4]. The amino acids play an important role in non linear optical crystals. The semi organic NLO materials are generally have a high nonlinear coefficient, high laser damage threshold, high thermal stability and mechanical strength than inorganic crystals [5-6]. In this connection, amino acids are prominent materials for NLO applications, as they contain zwitterions, which create the hydrogen bonds used for the generation of non centro symmetry structures favorable for attractive SHG properties of crystal [7-9]. A dipolar nature exhibits the peculiar physical and chemical properties in amino acids and these properties make them to ideal candidates for NLO applications.

In this present investigation, L-Valine Cadmium Chloride Crystal (LVCC) doped with Zinc chloride has been grown from its aqueous solution by slow evaporation method. The crystal has been characterized by powder XRD, FTIR, TGA/DTA and UV-Visible. The Kurtz powder SHG test was performed to confirm the second order non linearity of the grown crystal.

II.CRYSTAL GROWTH

L-Valine and Cadmium Chloride has been taken in an equimolar ratio of 1:1 and was dissolved in deionized water. 1M of Zinc chloride has been added slowly. The solution was stirred continuously using a magnetic stirrer for six hours to yield a homogeneous mixture. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation after a period of 30 days. The chemical equation governing the reaction is,

$C_5H_{11}NO_2 + CdCl_2.H_2O+ZnCl2 \rightarrow Cd\ [C_5H_{11}NO_2]\ Cl_2.\ ZnCl_2.\ H_2O$

III.EXPERIMENTAL DETAILS

The LVCC crystal doped with Zinc chloride was subjected to powder X-ray diffraction studies. Powder X-ray diffraction pattern was undertaken by X-ray diffractionmeter (Model JDX 8030) with CUKα (λ = 1.5418Å). The presence of functional groups has been confirmed with the help of Perkin Elmer FTIR spectrometer in the range of 400 to 4000 cm^{-1} using KBr pellet technique. The thermal decompositions of crystals were investigated by using Q500 V20.10 Build 36 meter. The optical transmission spectrum of LVCC crystal doped with zinc chloride was investigated by λ35 model Perkin Elmer double beam uv-visible spectrometer in the range of 200nm to 1000nm.

IV.RESULTS AND DISCUSSIONS

Powder XRD Analysis

The powder XRD pattern of LVCC crystals doped with zinc chloride is shown in fig.1. The sharp and sensitive peaks confirmed the crystalline nature of the grown crystal. The highest intense peaks of the observed powder XRD pattern has been compared with the standard XRD pattern of L-Valine (JCPDS file no.33-1954) and is indexed.

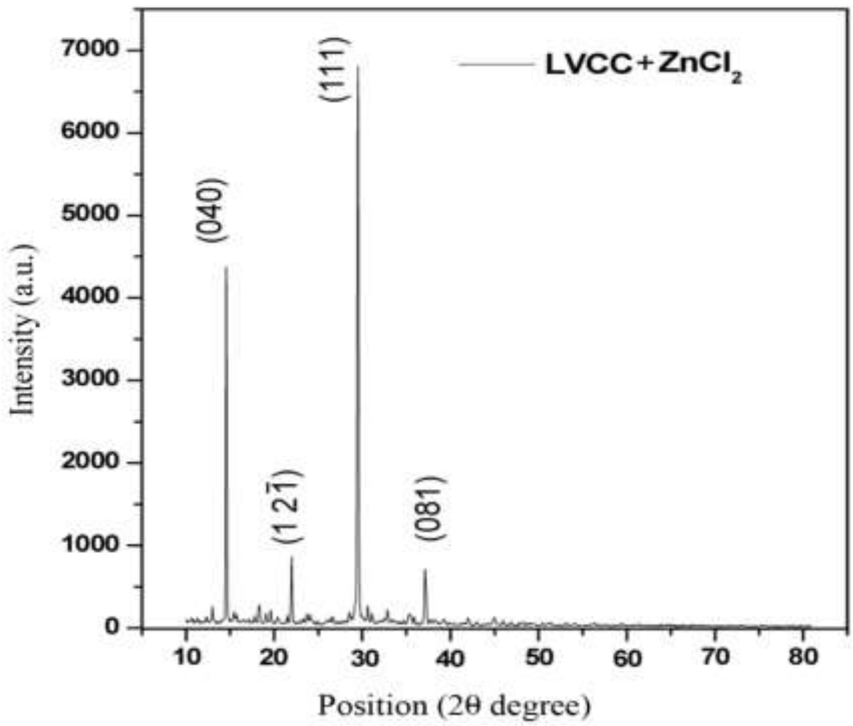

Fig.1The powder XRD pattern of the grown LVCC crystal doped with zinc chloride

FTIR Analysis

The FTIR spectrum of the LVCC crystal doped with the zinc chloride is depicted in fig. 2. The medium band at 2950 cm^{-1} is due to the NH_2^+ symmetric stretching vibration. The band at 2628cm^{-1} corresponds to N-H-O valence stretching combination. The medium band observed at 2109 cm^{-1} is assigned to C-O-C stretching vibration. The strong bands at 1587 and 1510 cm^{-1} are correlated to COO^- asymmetric stretching and NH_3+ symmetric deformation respectively. The medium bands occur at 1394 and 1328 cm^{-1} are attributed to COO^- symmetric stretching and C-O stretching respectively. The weak bands at 1271 and 1179cm^{-1} are attributed to CH_3 deformation and C-C stretching respectively. The peaks observed at 1065 and 1031 cm^{-1} are most probably due to the C-C-N stretching. C-H out of plane bending produces peaks at 824, 716 and 664 cm^{-1} respectively. The CH_2 and NH_3+ rocking have been appeared at 947 and 896 cm^{-1} respectively. The strong band appeared at 543 cm^{-1} may be due to C-CO deformation. The mode of vibration such as C-C deformation and COO^- rocking occur at 476 and 431 cm^{-1} respectively. The FTIR assignments of LVCC crystal doped with zinc chloride have been tabulated in Table 1.

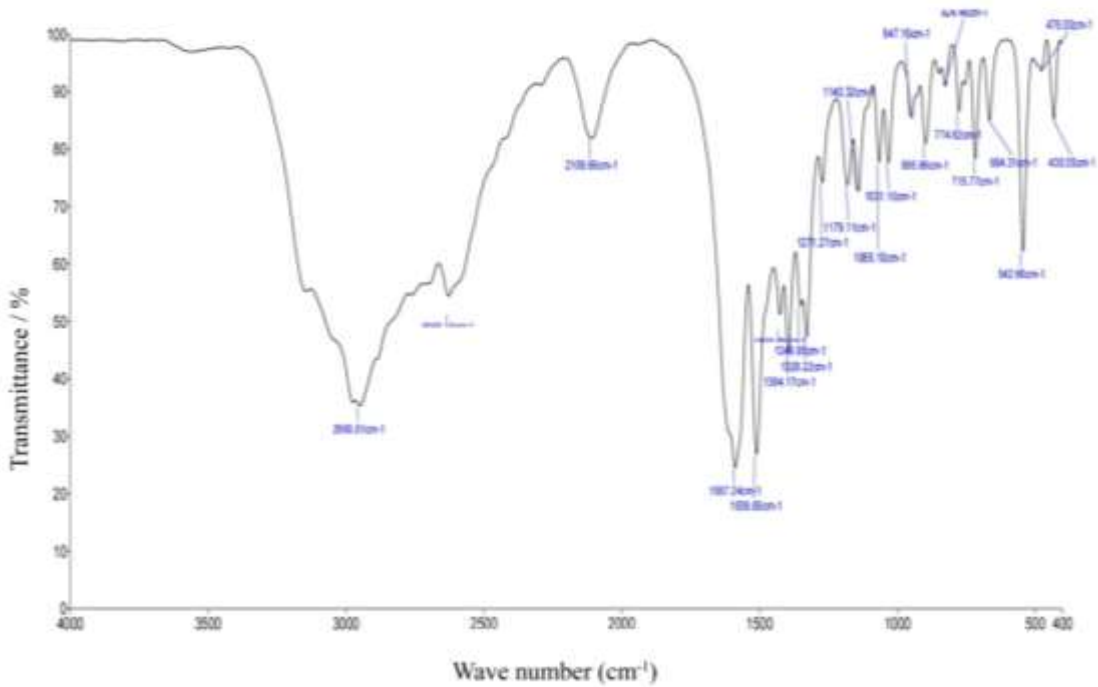

Fig.2FTIR spectrum of LVCC crystal doped with zinc chloride

Table 1 FTIR Assignments of LVCC crystal doped with $ZnCl_2$

L-Valine (cm^{-1})	L-Valine Cadmium Acetate (cm^{-1})	LVCC+$ZnCl_2$ (cm^{-1})	Assignments
2976	2973	2950	NH_2+ symmetric stretching vibration
2629	2626	2628	N-H-O valence stretching combination
-	-	2109	C-O-C stretching vibration
1585	1578	1587	COO^- asymmetric stretching
1507	1509	1510	NH_3+ symmetric deformation
1396	1394	1394	COO^- symmetric stretching
1329	1327	1328	C-O Stretching
1271	1270	1271	CH_3 deformation
1178	1180	1179	C-C Stretching
1065	1061	1065	C-C-N Stretching
1028	1021	1031	C-C-N Stretching
949	943	947	CH_2 Rocking
894	-	896	NH_3+ rocking bending
824	816	824	C-H out of plane bending
775	771	775	C-C Skeletal stretching
716	710	716	C-H out of plane bending
664	665	664	C-H out of plane bending
542	541	543	C-CO deformation
471	481	476	C-C deformation
428	432	431	COO^- rocking

Thermal Analysis

To analyze the thermal stability, melting point and phase transition of zinc chloride doped L-Valine cadmium chloride crystal, the thermogravimetric analysis and differential thermal analysis was carried out. The thermo gram of the grown LVCC crystal doped with Zinc Chloride is shown in Fig. 3. The TGA curve shows that there is no weight loss below 250°C, illustrating the absence of the absorbed water in the crystal. The major weight loss (87%) in the compound occurs in between 250-290°C associated with the liberation of L-Valine molecules. From the DTA curve it is reported that the sharp endothermic peak appear at 281.5°C is assigned as the melting point of the crystal. In between 290°C – 550°C the second major weight loss (10%) occurs due to the liberation of cadmium and other volatile substances.

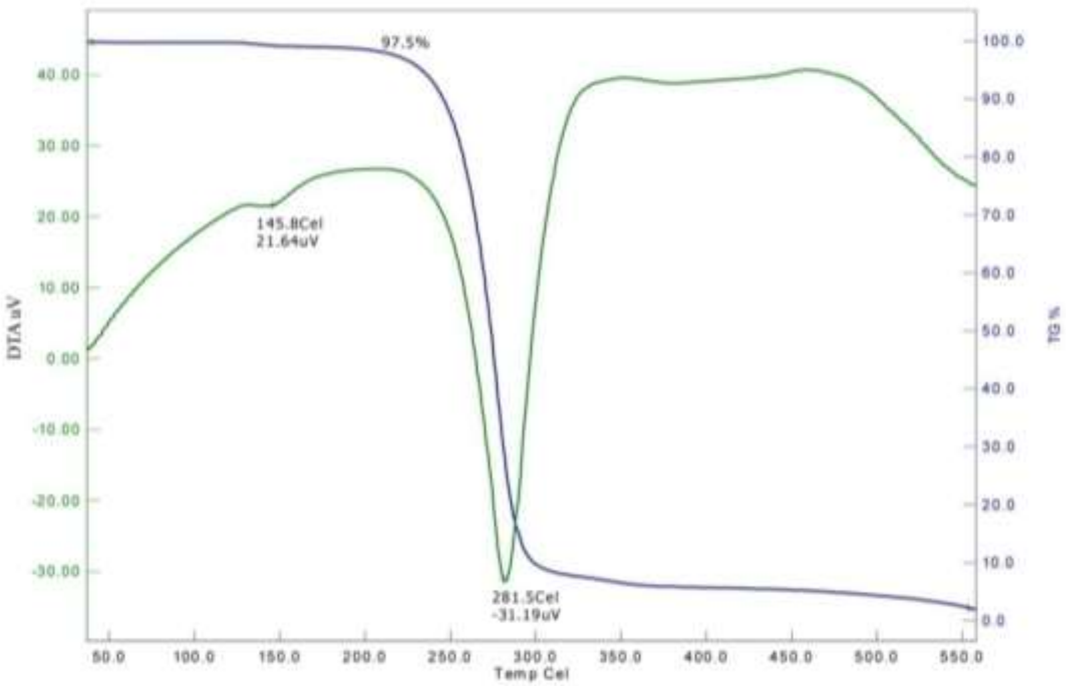

Fig. 3. TGA/DTA spectrum of LVCC crystal doped with zinc chloride

UV – spectral Analysis

The optical transmittance spectrum of the grown LVCC crystal doped with zinc chloride crystal is shown in fig.4. The grown crystal exhibits transmittance in entire visible region with a lower uv cut of wavelength around 245 nm. This property attests the suitability of the crystal for nonlinear applications [10].

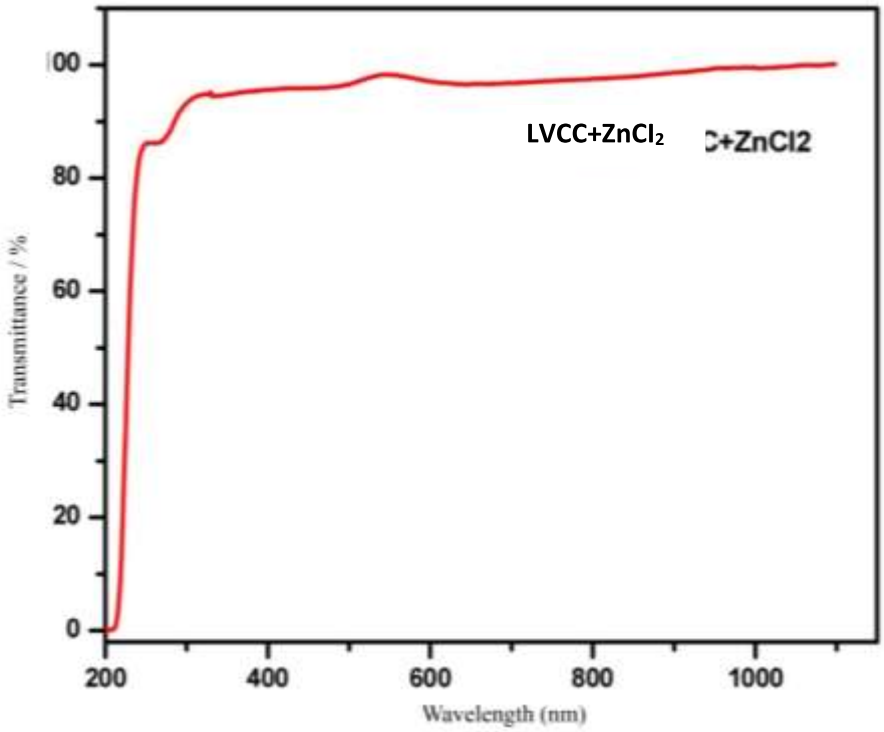

Fig. 4 The optical transmission spectrum of the grown LVCC crystal doped with zinc chloride

NLO studies

The SHG property of the grown crystal was studied using a Q-switched Nd-YAG laser by employing Kurtz powder test. The fundamental beam of an Nd-YAG laser with 1064 nm wavelength, pulse duration of 35ps and 10Hz repetition rate is focused on to the powdered sample. The SHG signal at 532 nm is recorded on the sample using a photo multiplier tube and boxcar average. The emission of green light confirms the presence of second order NLO activity in the crystal. The output of SHG signal (15.18 mJ) for the input energy of 0.7 J confirms the nonlinear behaviour of the crystal and was found to be 0.82 times that of KDP.

V.CONCLUSION

The title compound L-Valine Cadmium Chloride (LVCC) crystal doped with zinc chloride has been grown by the conventional slow evaporation technique. The sharp peaks from the observed powder XRD pattern of LVCC doped with zinc chloride crystal confirmed the crystalline nature. The functional groups present in the compound has been explained on the basis of FTIR studies. From the DTA curve it is reported that the melting point of the crystal is found as 281.5ºC. The UV cutoff wave length has been found out as 245 nm. All characterization properties revealed the NLO application of grown crystal.

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