Nonlinear Optical Properties of Glycine Cadmium Chloride(Gly-Cdcl2) Single Crystals

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Abstract— Glycine Cadmium Chloride (Gly-CdCl2) was synthesized by the slow evaporation method. The crystal structure of the sample was studied by single crystal and Powder X-ray diffraction. The UV transmittance spectra of the grown crystals indicate a good transparency of the crystals (190-1100nm). FTIR analysis was done to confirm the presence of various functional groups in the Gly-CdCl2 crystalline sample. The second harmonic conversion efficiency was determined using the Kurtz powder technique. The mechanical properties of the crystals show that this material belong to the category of soft materials.

Key words: Second Harmonic generation, powder X-ray Diffraction, Hardness studies

I. Introduction

There is considerable interest in the synthesis of new material with large second order optical nonlinearities, because of their potential for use in applications including telecommunications, optical computing, optical data storage and optical information processing1,2. Organic crystals have advantage over inorganic crystals, since they are optically more nonlinear. Large variety of organic materials can be synthesized according to some design principles. The organic molecules often formed by the hydrogen and weak vander waals bonds, hence possess high degree of delocalization. The NLO effect can be explained by strong donor-acceptor intermolecular interaction due to delocalized л electron and the ability to crystallize in non-centrosymmetric structure. The NLO materials with large intensity dependent refractive index and absorption coefficient are useful in device applications. These parameters determine whether intense beam undergone self-focusing or defocusing as it propagates in the material medium3. Traditionally, crystals of organic materials have been grown from the melt4,5 or from vapor6 or solution7,8. Some complexes of Glycine have been recently crystallized and various studies have been investigated by many researchers.

In this paper, we report the bulk growth and characterization studies of Glycine Cadmium Chloride (Gly-CdCl2) single crystal. Glycine is an efficient organic NLO Compound under the amino acid category.

A. Experimental Technique:

The commercially available reagent Glycine was purified by repeated crystallization using deionized water as the solvent.Gly-CdCl2 was synthesized by dissolving an equimolar ratio of recrystallized Glycine and Cadmium Chloride in double distilled water and stirring well 2 h using a magnetic stirrer and mixer was filleted by Watt man filter paper .Finally purified solution was kept at room temperature. The grown crystal was harvested after a typical growth period of 30 days. The grown crystals is shown in figure 1

Fig. 1: Photograph of the grown Gly-CdCl2 single crystals

B. Characterization Studies:

1) UV-Visible Studies:

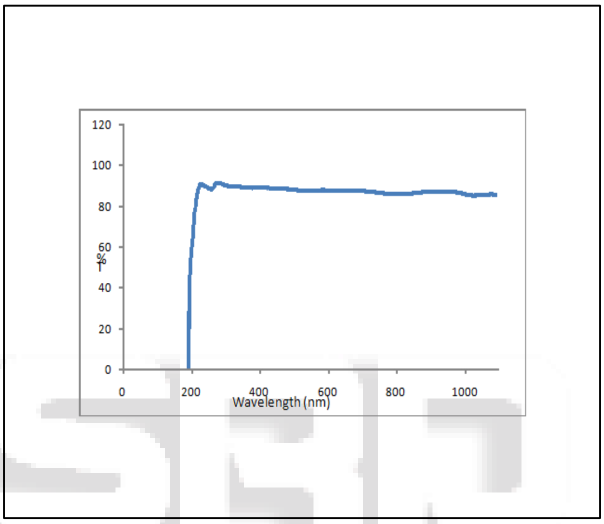

Fig. 2: UV–Vis spectrum of Gly-CdCl2 single crystal.

The UV-vis-NIR transmittance spectrum is shown in figure 2. It was recorded with SHIMADZU

UV-2501 IC, UV-Vis spectrometer in the range 190-1100 nm. The crystal shows a good transmittance in the visible region. The cut-off wavelength is around 220nm. It is observed that there is no significant absorption in the range 200-1100nm. Low absorption in the entire visible and near infrared region with the low –cut off wavelength at 220nm suggests that the material is quite suitable for SHG generation and other related optoelectronic applications. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices[9,10].

C. Fourier Transform Infrared (FTIR) Analysis:

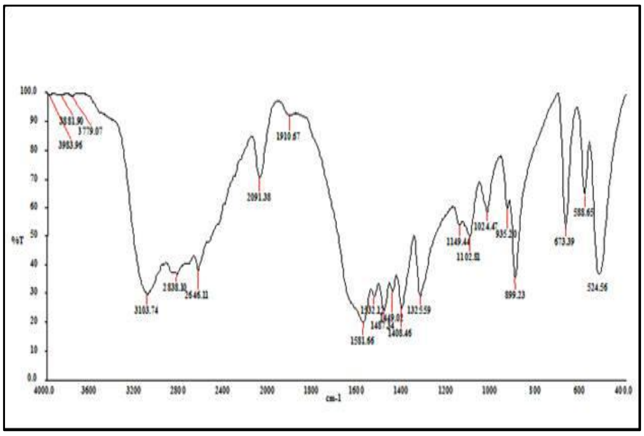

Fig. 3: FTIR spectrum of Gly-CdCl2 single crystal

Wavenumber(cm^{-1})	Band Assignments
3103	N-H stretching vibrations
2846	C-H stretching
1487, 1325	Asymmetric modes of COO^-
1408	Asymmetric C=S stretching
1532,1449,1149	NH_3^+ stretching
1024	N-C-N stretching
935	CN Symmetric
899	C-C symmetric stretching
673	NH_2 deformation
588,524	NH_3^+ torsion

Table 1: Assignments of vibrational frequencies of the grown crystals.

D. Powder X-Ray Diffraction Analysis:

The fine power of the title compound has been subjected to powder X-ray diffraction analysis and the recorded pattern is shown in figure 4. The powder sample was scanned in steps of 0.1° for a time interval of 10 seconds over a 2ϴ range of 10° to 70°. The sharp and well defined Bragg's peaks at specified 2ϴ angles show the crystalline nature and purity of the crystal. New peaks in the XRD pattern of the grown crystal confirm the incorporation of cadmium chloride in the grown crystals.

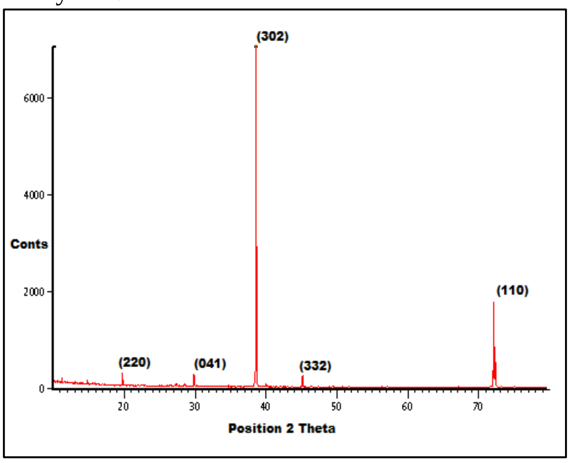

Fig. 4: Powder X-ray Diffraction pattern of Gly-CdCl2 single crystal.

E. Single Crystal X-Ray Diffraction Analysis:

The single crystal X-ray diffraction analysis was carried out using ENRAF NONIUS CAD4 single crystal X-ray diffractometer. The obtained lattice parameters of Gly-CdCl2 crystals are given in the table 1.

Parameters	Gly-$CdCl_2$
a	8.274 Å
b	9.058 Å
c	13.743 Å
α	90 Å
β	106.16 Å
γ	90 Å
Space group	$P2_1/C$
Crystal structure	Monoclinic

Table 2: lattice parameters of the grown crystals.

F. Microhardness Studies:

Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indentor. A well polished Gly –CdCl2 crystal of 2 mm thick was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The indentation time was kept as 5s for all the loads. The hardness was calculated using the relation Hv = 1.8544 P/d2 kg/mm2, where P is the applied load in g and d is the diagonal length of the indentation impression in millimetre. The relation between hardness number (Hv) and load (P) for Gly –CdCl2 is shown in Fig. 5. The hardness increases gradually with the increase of load and above 100 g cracks were developed on the smooth surface of the crystal due to release of the internal stresses generated locally by indentation11. The relation between load and size of the indentation is given by well known Mayer's law P = adn. Here a and n are constants depending upon the material. By plotting log (P) versus log (d) Fig. 6, the value of the work hardening coefficient (n) was found to be 1.6324. According to Onitsch, 1.0≤n≤1.6 for hard materials and n > 1.6 for soft materials12. Hence, it is concluded that Gly –CdCl2 crystal is a soft material.

S.No.	Hv kg/mm^2	$C_{11}\times10^{14}$ Pa
1	20.5	1.97
2	34.55	4.92
3	52.3	10.17

Table 3: Elastic Stiffness Constant for Different Load

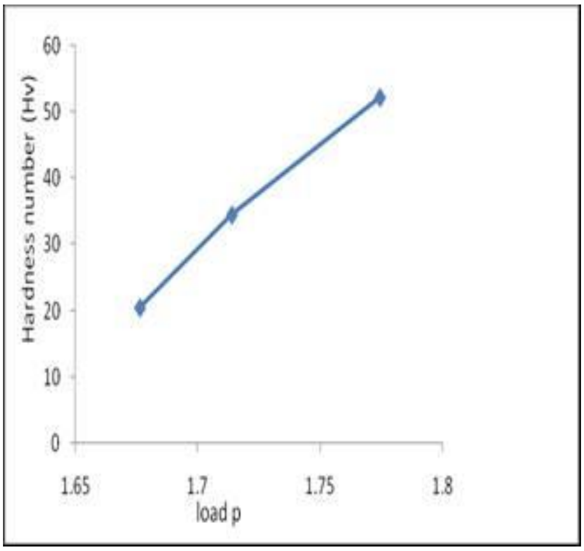

Fig. 5: Variation of load p with Hardness number Hv.

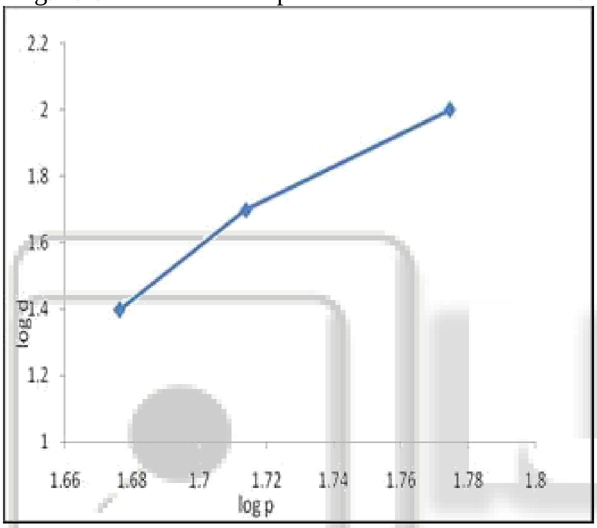

Fig. 6: Variation of log(P) with log(d).

G. Second Harmonic Generation:

The NLO property of the crystal was confirmed by the KurtzPerry powder technique. The crystals are ground to powder and packed between two transparent glass slides. The first harmonic output of 1064nm from a Nd:YAG laser was made to fall normally passed through the Gly –CdCl2 powder sample after reflection from an IR reflector. The SHG behavior in these crystals was confirmed from the emission of intense green radiation (λ = 532 nm) by the sample. The result obtained shows that the powder SHG relative efficiency of Gly –CdCl2 crystal is about 0.68 times that of potassium dihydrogen orthophosphate (KDP). As the second order nonlinear efficiency will vary with the particle size of the powder sample, higher efficiencies are expected to be achieved by optimizing the phase matching 13.

II. CONCLUSIONS

A good quality crystal was obtained in a period of 30 days by slow evaporation method.

UV-Vis-IR spectrum confirming the transparent nature in the visible region.FTIR confirms the identity of the grown crystals. Powder XRD studies confirms crystalline nature and single crystal X-ray diffraction shows grown crystals belongs to monoclinic system. The microhardness studies reveal that the mechanical strength of the crystal is soft material it used for device fabrication. The grown crystals have responded well for second harmonic generation efficiency (SHG) .it is 0.68 times that of potassium dihydrogen orthophosphate (KDP).

REFERENCES

[1] Hiroaki Adachi,Y.Takahashi,Junko Yabuzaki,Yusuke Mori,Takamoto Sasaki,J.Crystal Growth,198-199 &568,1999.
[2] Marder .S.R, Perry.J.W and Yakymyshyn.C.P,Chem.Mat .6,1994.
[3] Prasad PN, Williams DJ, Introduction to Nonlinear Optical Effects in Molecules and Polymers,Wilely,New York,1991.
[4] McArdle,B.J,Sherwood.J.N,Damask.A.C,J.Crst.Growth ,22,193-200,1974.
[5] Aravanandhan.M,Sankaranayanan.K,Ramasamy.P,Sanjeevaraja.C, and Ramamoorthy.K,Thin Film ,2-7,2005.
[6] AyersS,Faktor.M.Man.D,Stevensons.j,Mater.Sci,7,31,1972.
[7] Aggarwal.M.D,Lal.R.B,Rev.Sci.Instrum,14,772-773,1983.
[8] Hampton.E.M,Shah.B.S,Sherwood.J.N,J.Cryst.Growth, 22-28,1974.
[9] Roshan.A, Cyriac Joseph.S, Mater. Lett. 49 , 299–302,2001.
[10] Venkataramanan.V, Maheswaran.S, Sherwood.J.N, H.L. Bhat, J. Cryst. Growth 179, 605–610,1997.
[11] Theresita Shanthi.N, Selvarajan.P, Mahadevan.C.K, Curr. Appl. Phys. 9 ,1155–1159, 2009.
[12] E.M. Onitsch, Mikroscopia 2 , 131–151, 1947.
[13] Ravindra H.J, Suresh Kumar. M.R, Rai.C, Dharmaprakash. S.M, J. Cryst. Growth ,294, 318-322, 2006.

