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Growth and characterization of Glycine doped Zinc Chloride crystals for NLO applications

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ABSTRACT

Semi-organic nonlinear optical crystal of Glycine Zinc Chloride (GZC) crystals were grown by slow evaporation solution growth technique. The crystal system and lattice parameters were determined from the single crystal X-ray diffraction analysis. Fourier transform infrared (FTIR) studies confirm the various functional groups present in the grown crystal. The transmittance and absorbance of electromagnetic radiation is studied through UV-Visible spectrum. The mechanical property of grown crystals has been analyzed by Vicker's micro hardness method. The thermal behaviour of the grown crystals has been investigated by DTA and TGA analysis.SHG efficiencies were measured using Kurtz powder technique. GZC has the NLO efficiency of 72% of KDP crystal.

1. Introduction

Zinc chloride ($Zncl_2$) is inorganic salt that belongs to orthorhombic crystal system. Its space group is Fm3m. It is used in medicine in treatment of hypokalemia and food processing. Some organic and inorganic crystals are grown for its NLO effect [1-2]. In semi-organics, polarisable organic molecules are stoichiometrically bound within an organic host [3]. Nowadays amino acids are noticeable materials due to its component nonlinear optical efficiency. Some complexes of amino acids with inorganic salts have already been reported by many researchers [4,5], and that has proven to be a good candidate for nonlinear optical applications. Recent interest is focused on the development of new materials with improved properties [6]. Glycine, NH_2CH_2COOH, the simplest of the 20 protein amino acids, functions as a neurotransmitter and is one of the principle components of structural proteins, enzymes and hormones. Glycine is one of the non-essential amino acids and is used to help create muscle tissue and convert glucose into energy. It is also essential to maintaining healthy tissues in all parts of the body. Glycine is the only protein forming amino acid without a centre of chirality. From this motivation the author select amino acid as dopant in this research work. The grown crystals were subjected to different characterizations.

2. Experimental

The saturated solution of Zinc chloride was prepared at room temperature from the recrystallized salt of Zinc chloride and double distilled water. The solution was then filtered to remove the suspended impurities. 0.1 mol % of Glycine was added with this saturated Zinc chloride solution. Again the solution was filtered by using filter paper. The filtered solution was closed with thin perforated plastic sheet and the solution was placed in a vibration and dust free atmosphere.

Good transparent single crystals were formed due to the evaporation of solution at room temperature. The grown crystals were harvested from the solution after five days. Fig.1 shows the as-grown single crystal of GZC. The grown crystal was subjected to different characterization analyses in order to know its suitability for applications.

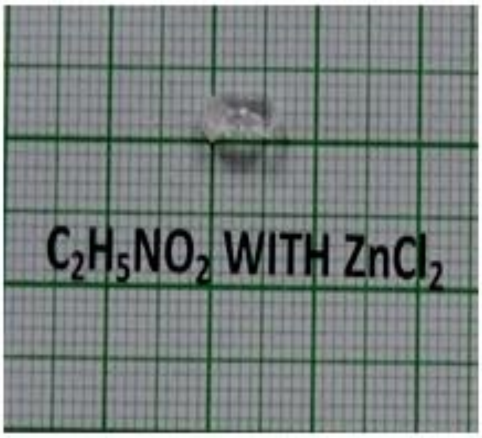

Fig 1. Glysine doped Zinc chloride

3. Results and discussion

3.1Single crystal X-Ray Diffraction Analysis

The single crystal X-ray diffraction analyses of Glycine doped zinc chloride crystals (GZC) were performed using Bruker Kappa APEX II single crystal X-ray diffractometer. It is observed that GZC crystals crystallize in the orthorhombic system with the space group Fm3m. The obtained lattice parameter values confirmed that the addition of Glycine did not change the orthorhombic structure of Zinc chloride. The lattice parameters are tabulated in table.1.

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Table 1. The lattice parameter values

Lattice parameter	GZC crystal
a(Å)	11.205
b(Å)	15.207
c(Å)	15.550
Volume a(Å)	2649.6

3.2. UV–Vis analysis

Optical absorption spectra of Glycine doped crystal were recorded using Jasco - Vis NIR model V-670 spectrometer in the range 200-800 nm. The recorded absorption spectrum was shown in Fig. 2. The cut-off wavelength (λ_{max}) of the grown crystal is taken as the point at which absorbance drastically falls to zero. This study indicates that the UV cut-off wavelength of the crystal has 230 nm and there are no significant absorptions observed in the entire region of the spectrum. Transmittances of doped crystal were maximum in the region of 250 nm to 800 nm. It is an important requirement for optical quality of the crystal. The wide transparency in the entire visible region is one of the additional key requirements for having efficient NLO character [8].

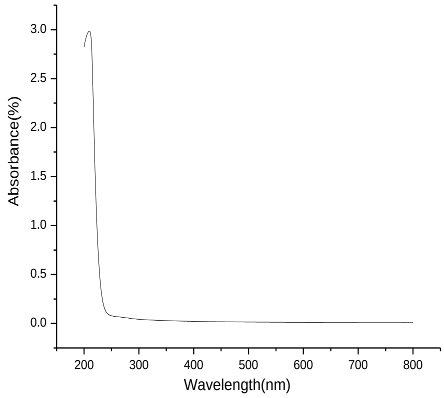

Fig 2. Optical absorption spectra of GZC crystal.

3.3. FTIR spectral analysis

The FTIR spectral analysis of doped crystal were carried out between 25 cm^{-1} and 2000 cm^{-1} using Shimadzu model IR Perstege-21 spectrophotometer and are shown in Fig. 3. The FTIR spectrum provides information about the molecular structure of the compound, modes of vibration and the presence of functional groups [Table.2]. The functional groups were identified and assigned for GZC crystal. The strong peak at 1319 cm^{-1} is assigned to C-O stretching of GZC crystal and 1031 cm^{-1} is due to C-N stretching. The peak at 1128 cm^{-1} is assigned to NH_2 deformation. The peaks appearing at 592 cm^{-1} are due to COO^- wagging.

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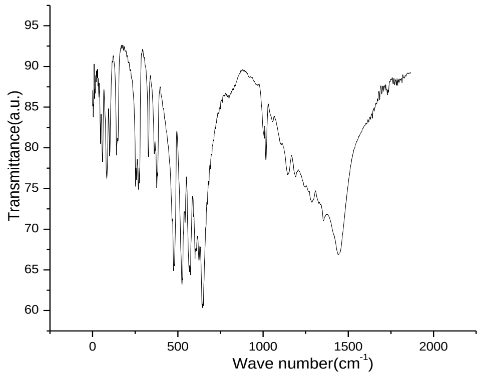

Fig 3. The FTIR spectrum of GZCcrystal.

Table 2. Vibrational assignments of pure and doped Zinc chloride crystals.

S.No	Observed FTIR frequencies (cm^{-1}) for GZC crystal	Vibrational assignments
1	511	COO rocking
2	559	COO rocking
3	592	COO wagging
4	673	COO inplane deformation
5	891	C-C Stretching
6	925	NH_3^+roking
7	1031	C-N Stretching
8	1128	NH_2 deformation
9	1319	C-O Stretching
10	1411	C=O ring Stretching
11	1444	--
12	1500	CH_2 bending
13	1562	C-O Stretching
14	1602	-C=O Carboxylate ion asymmetric stretching
15	1643	Carboxylate group C=O asymmetric stretching

3.4. Thermal analysis

Thermo gravimetric and differential thermal analyses gives, information regarding phase transition and different stages of decomposition of the crystal system. Thermal properties of the grown crystals were studied by using Siint model TG/DTA- 6200. The analyses were carried out between 30°C and 800°C in the nitrogen atmosphere at a heating rate of 20°C min^{-1}. The TGA and DTA curves of amino acid doped crystal are shown in Figs. 4 and 5 respectively. The weight loss starts at 80°C. At 246°C sudden decomposition takes place.

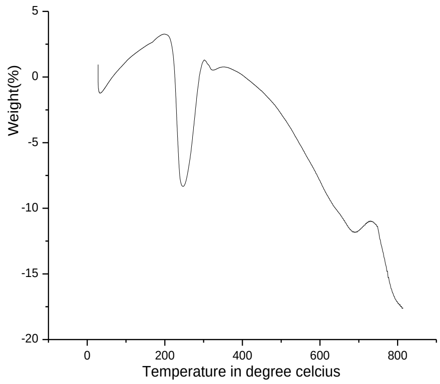

Fig 4.DTA spectrum of GZC crystal.

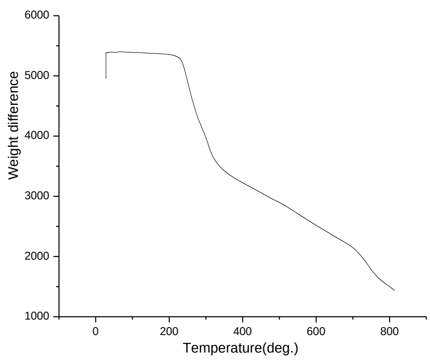

Fig 5.TGA spectrum of GZC crystal.

3.5 Second harmonic generation efficiency measurement

The second harmonic generation conversion efficiency of the samples was measured using Kurtz powder technique. A Q switched ND:YAG laser beam of wave length 1064 nm was used within an input energy of 5.02 mJ/pulse and the pulse width of 8 ns the depletion rate being 10 Hz. The SHG radiations of 532 nm (green light) emitted were collected by a photo multiplier tube (PMT-Philips Photonics model 8563) and the optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052). The SHG values were found to be 72% of KDP crystals.

3.6. Fluorescence studies

The spectrum recorded by the emission of photo generated minority carriers is a direct way to measure the band gap energy. The emission spectra of GZC crystal were recorded in the range 240-700 nm using Perkin Elmer model LS-45 Spectrofluorometer. Fig.6. shows the emission spectrum of GZC crystals. Band gap energy of GZC crystals were calculated using the formula $E_g = hc/\lambda e$. Where h, c and e are constant λ is the wavelength of fluorescence. The calculated band gap energy of GZC crystal is 3.1835 eV. It concludes the crystal have better fluorescence effect.

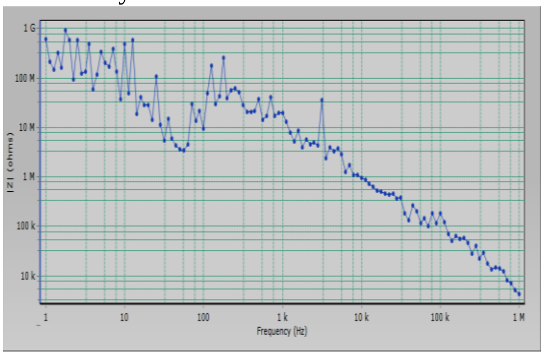

Fig 6. Fluorescence study of GZC crystals.

3.7. Micro-hardness measurements

The good qualities of single crystals needed for device fabrication not only depends on optical performance but also on their mechanical behaviours Vickers micro hardness test is one of the best methods to understand the mechanical properties of the materials such as brittleness and cracking. Doped crystals were subjected to Vickers micro hardness test using Shimadzu model HMV-2T micro hardness tester. The indentations were made on the surface of the grown crystals by varying the load from 25 g to 100 g at room temperature with a constant indentation time of 5s. The graph plotted with load and Hardness number is shown in Fig. 7. When load increase hardness number also increases.

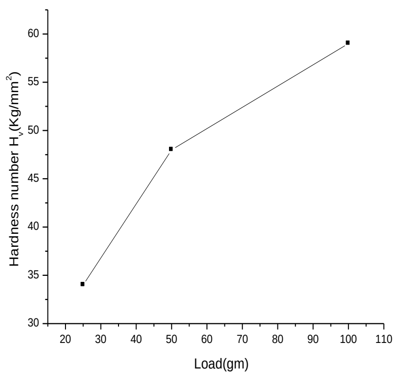

Fig 7. Vicker's hardness number for GZC crystal.

3.8. Scanning electron microscope analysis

Scanning the surface with a high energy beam of electrons in a raster scan pattern is called Electron microscope. The shape and size of the particles making up the object can be viewed and studied. Scanning electron microscopy (SEM) was performed using the Jeol model JSM – 6390. Fig.8 shows the SEM images of the as grown GZC crystal. The SEM micrographs show the purity and crystalline nature of the grown crystals. It is seen from the SEM pictures that the surface of the as grown crystal is smooth and highest clarity.

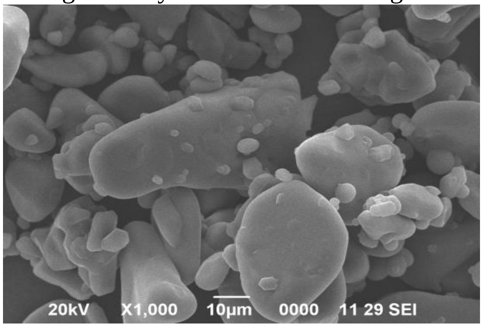

Fig: 8 SEM image of GZC Crystal

3.8. Energy dispersive X-ray analysis

The Energy dispersive X-ray analysis (EDAX) was performed using the Jeol model JSM – 6390.The EDAX spectra for GZC crystal were shown in Fig.9 and Fig.10. The elements were identified and presented. From EDAX spectrum the chemical composition weight has been calculated. The estimated % of C, N, O, Cl and Zn of GZC crystal are shown in table 3.

Table 3. The estimated % of C, N, O, Cl and Zn in GZC crystal.

Element	Weight%	Weight%	Weight%
C	31.35	2.71	43.23
N	23.16	3.65	27.39
O	19.63	1.54	20.33
Cl	11.73	0.71	5.48
Zn	14.13	0.93	3.58
Total	100.00		

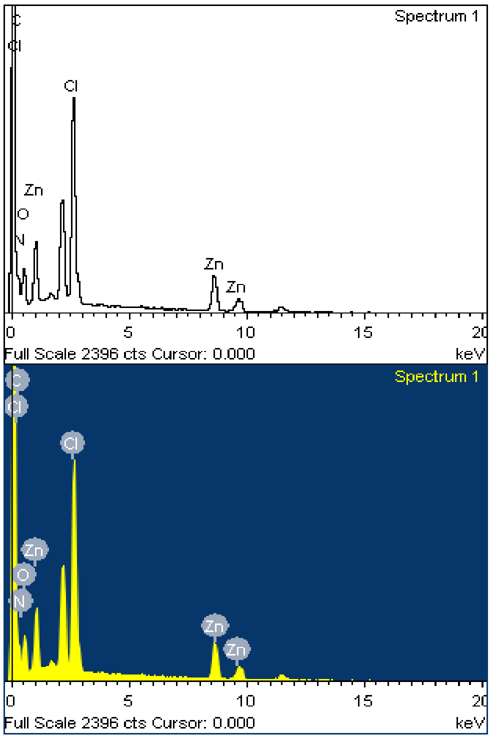

Fig.9 and Fig.10: The EDAX spectra for GZC crystal

4. Conclusion

Glycine doped Zinc Crystals (GZC), a semi-organic NLO material, has been grown from aqueous solution. Lattice parameters have been evaluated by Single crystal XRD analysis. The presence of various functional groups of the grown crystals has been identified by FTIR spectral analysis. GZC has 72% of SHG efficiency compared with KDP. The Energy dispersive X-ray analysis (EDAX) proves the elements present in the crystal. TGDTA and the micro hardness study also show the thermal stability and mechanical strength of the as grown crystal. The SEM micrographs show the purity and crystalline nature of the grown crystals.

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