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GROWTH AND CHARACTERIZATION OF GAMMA GLYCINE SINGLE CRYSTALS GROWN FROM Cu-DOPED GLYCINIUM OXALATE (CGO) BY SLOW EVAPORATION PROCESS

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ABSTRACT
Cu-doped Glycinium oxalate (CGO) single crystals have been grown by slow solvent evaporation process. The grown crystals were subjected to different characterization studies like single crystal X-ray diffraction (XRD), Fourier transform infrared (FTIR), Ultraviolet-visible (UV-vis) absorbance and Photoluminescence (PL) emission studies. From the single crystal XRD results, it shows that gamma glycine single crystal grown from CGO crystallizes in the hexagonal structure. The presence of functional groups in the as-grown crystal was confirmed from the FTIR studies. The optical transparency and luminescence behavior of the grown gamma glycine crystal were investigated from the UV-absorption and PL studies.

KEYWORDS: Gamma glycine; CGO; Single crystals; Slow-evaporation process; Optical properties.

1. INTRODUCTION
In the crystal growth technology, it is well-proved that the amino acid-based crystal exhibits variety of applications in the fields of electronic communication and laser technology [1-3]. Among all the amino acids, glycine is one of the most common simplest amino acid, which is found in the protein of all living organisms. Meanwhile, the glycine crystallizes in three distinct polymorphs at ambient pressures known as α-glycine, β-glycine and γ-glycine [4-6]. Further, most of the dicarboxylic salts are reported to be active in second harmonic generation (SHG) and it may be useful to study complexes with carboxylic acid and their properties [7]. Oxalic acid is a reducing agent and its conjugate base, known as oxalate, is a chelating agent for metal ions. Anhydrous oxalic acid exists as two polymorphs; in one the hydrogen-bonding results in a chain-like structure whereas the hydrogen bonding pattern in the other form defines a sheet-like structure. Moreover, glycine can exist in zwitter ionic form; hence, it can form compounds with charged and uncharged chemical compounds. It results in the formation of glycine coordinated compounds. The carboxylic acid group of glycine forms salt when combined with amino group by donating protons. Glycine exists in the cationic forms with a positively charged amino group, while oxalic acid exists as the anion. In particular, doped organic crystals have been attracted much attention due to their ability to form variety of optical devices applications. Further, organic based materials can exhibit higher nonlinear optical efficiencies than those of inorganic materials due to large optical susceptibilities, high optical threshold for laser power and low frequency dispersion [8]. The charge transfer complex of glycine and oxalic acid-glycinium oxalate crystallizes in the monoclinic system with a space group $P2_1/c$, which is a centro-symmetric system. In order to modify and improve properties for application, the dopants have been tried in glycinium oxalate crystals [9-10]. In this work, we have carried out the material synthesis, growth and characterization of the gamma glycine single crystals from CGO by slow evaporation process. The structural and optical properties of the grown gamma glycine crystals are characterized by single crystal XRD, FTIR, UV absorbance and PL emission analysis.

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2. MATERIALS AND METHODS

The single crystals of Cu-doped Glycinium oxalate (CGO) were synthesized from slow evaporation process using water as a solvent. CGO was prepared by dissolving a stoichiometric (1:1) amount of glycine and oxalic acid in double distilled water and then followed by 2 mole % copper sulphate was added to the above saturated solution, until the equilibrium was established (pH=2). The temperature was maintained around 45°C to avoid any decomposition of element from the compound. The good qualities of as-grown crystals have been harvested in a span of three weeks as shown in Fig.1.

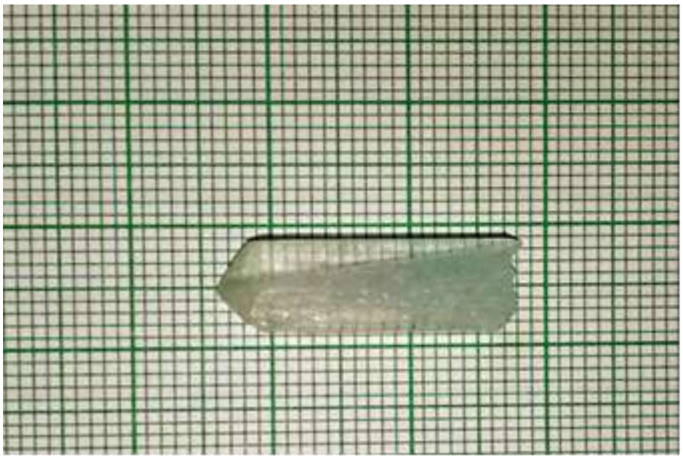

Fig.1 As grown CGO crystal

3. RESULTS AND DISCUSSION

a. Single crystal XRD analysis

Single crystal XRD analysis for the grown CGO crystal is carried out using Bruker X8 Kappa Apex-II X-ray diffractometer. The determined lattice parameter values are a=b=7.06 Å, c=5.50 Å, $\alpha = \beta = 90°$, $\gamma = 120°$and V= 237Å^3. From the results, it is observed that gamma glycine single crystal grown from CGO crystallize in the hexagonal structure, which is in good agreement with the reported values [11].

Table 1 Lattice parameters of CGO single crystals

Sample	Lattice Parameters						
	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
CGO	7.06	7.06	5.50	90.00	90.00	120.00	237

b. FTIR analysis

The FTIR spectrum of the CGO grown crystals are recorded using KBr pellet technique in the region 4000 to 400 cm^{-1} using a Bruker Model IFS 66V spectrometer. Fig.2 shows the FTIR spectrum of CGO crystal. In the high-energy region, there is a broad-like envelope between 2624 and 3142 cm^{-1} resulting from the hydrogen bonded symmetric and asymmetric stretching vibrations of NH_3^+ group [12–13]. The peaks at 2819, 2907 and 2981 cm^{-1} correspond to asymmetric and symmetric stretching vibration of COO^-. The peaks at 2624 and 1353 cm^{-1} are attributed to CH stretching vibration and CH_2 wagging, respectively. In addition, the band observed at 909 cm^{-1} is attributed to carboxylate groups while the absorption peak at 1144 cm^{-1} is attributed to NH_3^+ group. Further, the peaks located at 2981, 15622 and 1507 cm^{-1} can be assigned to the NH_3^+ stretching vibrations. The NH_3^+ stretching region shows broad band characteristics of hydrogen bonding. Thus, carboxyl group is present as carboxylate ion and amino group is present as ammonium ion in glycinium oxalate. The prominent peak located at 707 cm^{-1} can be attributed to the stretching of dopant metal ion, it confirms the presence of Cu^{2+} in the crystal lattice.

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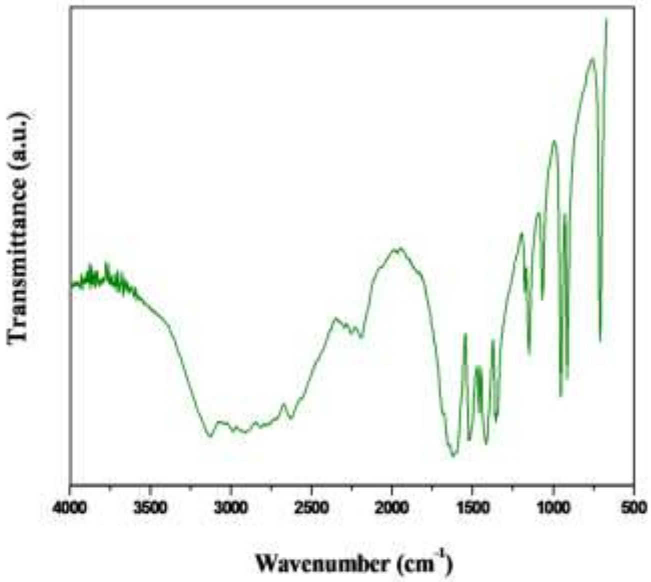

Fig.2 FTIR spectrum of CGO single crystal

c. Optical studies

The optical studies of the gamma glycine single crystals are characterized from the UV absorbance and photoluminescence analysis. The UV-vis absorption spectrum of as-grown gamma glycine crystal is recorded by using a Varian Cary 5E spectrophotometer as shown in Fig.3. It is clearly showed that the crystal has a transparency window from 350 to 800 nm, which makes it a potential material for blue light emission. From the UV absorption spectrum, the band gap energy value of the gamma glycine crystal is calculated to be 4.13 eV. The optical study depicts that very low absorption in the entire visible region, which is one of the desired characteristics for the device fabrication [14].

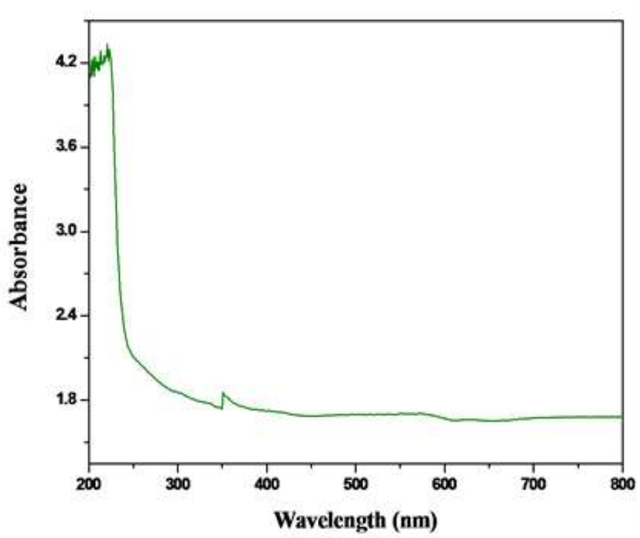

Fig. 3 UV-visible spectrum of gamma glycine crystal

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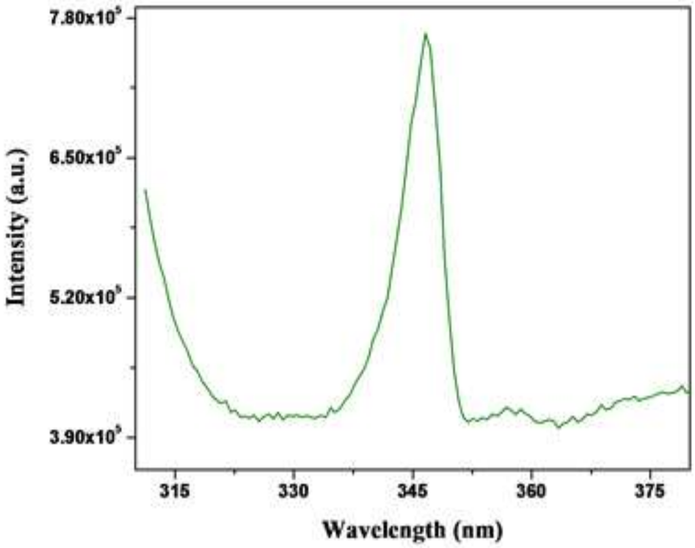

Fig. 4 PL emission spectrum of gamma glycine crystal

The room temperature photoluminescence (PL) emission spectrum of the gamma glycine crystal is recorded with fluorescence spectrometer (FLS920) using Xe lamp as the excitation light source. Fig. 4 shows the PL emission spectrum of gamma glycine single crystal with an excitation wavelength of 250 nm. From the PL spectrum, an intense and broad UV emission peak is found to be around 345 nm, which can be generated by the free exciton recombination. The high UV emission indicates a perfect crystal quality of the gamma glycine crystals. The significant luminescence property of the grown gamma glycine crystal may be interesting for further optoelectronic applications.

4. CONCLUSION

Single crystals of gamma glycine from Cu-doped Glycinium oxalate (CGO) have been successfully grown by slow evaporation solvent method. The hexagonal crystal structure of gamma glycine is determined from single crystal XRD analysis. The presence of various functional groups of CGO is identified from the FTIR analysis. The optical transparency and luminescence behavior of the grown gamma glycine crystal is confirmed by UV-absorption and PL studies. From the optical studies, it is concluded that the grown CGO crystal can be suitable for optoelectronic devices.

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