

GROWTH AND CHARACTERIZATION OF L-PROLINE DOPED GLYCINIUM OXALATE (LPGO) SINGLE CRYSTALS BY SLOW EVAPORATION PROCESS

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ABSTRACT-Good optical quality single crystals of L-proline doped glycinium oxalate (LPGO) are grown by slow evaporation method. The structural perfection of the grown LPGO crystals has been analyzed by high-resolution X-ray diffraction (HRXRD) measurements. The monoclinic structure of the grown LPGO is confirmed by using single crystal X-ray diffraction (XRD) analysis. The Fourier transform infrared (FTIR) spectrum of LPGO crystal confirms the presence of functional groups. From the UV transmission studies, the absence of absorption in the region between 200 and 800 nm is the key requirement for the materials having optical devices applications.

KEYWORDS- LPGO; Single crystals; Slow-evaporation process; Structural properties; Optical properties

1. INTRODUCTION

In the recent years, amino acid based crystals have wide applications especially in the fields of communication, laser technology thermal imaging and electronics [1-2]. 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 [3-4]. Glycine ($C_2H_5NO_2$) is the simplest amino acid with just a hydrogen atom as side chain. Amino acids, except glycine, are characterized by chiral carbons, a proton donating carboxyl ($-COOH$) group and the proton-accepting amino ($-NH_2$) group. Oxalic acid is an organic compound with molecular formula $H_2C_2O_4$. Glycine exists in the cationic forms with a positively charged amino group, while oxalic acid exists as the anion. The charge transfer complex of glycine and oxalic acid-glyciniium oxalate crystallizes in the monoclinic system with a space group $P2_1/c$, which is a centro-symmetric system [5-6]. In order to modify and improve properties for application, the dopants have been tried in glyciniium oxalate crystals [7].

In this work, we have done the material synthesis, growth and characterization of the organic compound of L-proline doped glyciniium oxalate (LPGO) single crystals by slow evaporation process. The grown LPGO single crystals are characterized by High resolution X-ray diffraction (HRXRD), single crystal XRD, Fourier transform infrared (FTIR) and UV transmission analysis.

2. MATERIALS AND METHODS

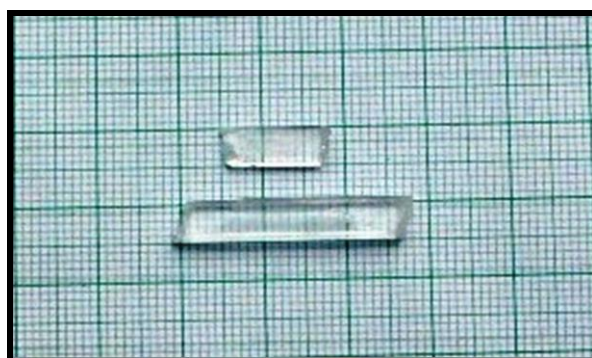


Fig 1: As grown LPGO crystal

All the chemical reagents with commercial AR purity are used directly without further purification. The single crystals of LPGO are synthesized from slow evaporation process using water as a solvent. LPGO is synthesized by dissolving a stoichiometric (1:1) amount of glycine ($C_2H_5NO_2$) and oxalic acid ($C_2H_2O_4$) in double distilled water and then followed by 2 mole % L-proline ($C_5H_9NO_2$) is added to the above saturated solution, until the equilibrium is established (pH=2). The temperature is maintained around 45°C to avoid any decomposition of element from the compound. Good quality of crystals has been harvested in a span of 2 weeks. The grown crystal of LPGO is shown in Fig.1.

3. RESULTS AND DISCUSSION

3.1. MULTICRYSTAL X-RAY DIFFRACTOMETRY

The crystalline perfection of the grown single crystals is characterized by High resolution XRD (HRXRD) by employing a multocrystal X-ray diffractometer developed at NPL [8]. The well-collimated and monochromated $MoK\alpha_1$ beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,-,-,+) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The rocking or diffraction curves are recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak so that all the meaningful scattered intensities on both sides of the peak include in the diffraction curve. The DC is recorded by the so-called ω scan wherein the detector is kept at the same angular position $2\theta_B$ with wide opening for its slit. This arrangement is very appropriate to record the short range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or due to low angle and very low angle structural grain boundaries [9].

Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the crystal and the possible layers which may sometimes form on the surfaces on crystals grown by solution methods [10] and also to ensure the surface planarity, the specimen is first lapped and chemically etched in a non-preferential etchant of water and acetone mixture in 1:2 volume ratio.

3.2. HRXRD ANALYSIS

Fig. 2 shows the high resolution X-ray diffraction curve recorded for (010) diffraction planes using $MoK\alpha_1$ radiation for a typical LPGO single crystal specimen. On careful observation, the curve does not seem to be a single peak. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains an additional peak, which is 105 arc sec away from the higher intensity peak. The additional peak corresponds to an internal structural low angle boundary. For a better understanding, the schematic of a structural grain boundary is given in the inset of Fig. 2. As seen in the inset two regions of the crystal are misoriented by a finite angle α also known as tilt angle. Tilt angle may be defined as the misorientation angle between the two crystalline regions on both sides of the structural grain boundary. The two regions may be perfect. If the value of α is ≤ 1 arc min, we may call it as very low angle boundary. If $\alpha > 1$ arc min but less than a deg, we call it as low angle boundary [9]. The angular separation between the two peaks gives the tilt angle α which is 105 arc sec for the specimen crystal as seen in the Fig.2. The FWHM (full width at half maximum) of the main peak and the low angle boundary are respectively 50 and 38 arc s. These relatively lower values reveal the fact that both the regions of the crystal are nearly perfect. These types of structural defects are probably generated in the crystals due to mechanical/thermal fluctuations occurred during the growth process and/or also due to fast growth [11]. It may be mentioned here that such minute defects could be detected with well resolved peaks in the diffraction curve only because of the high-resolution of the diffractometer, characterized by very low values of wavelength spread i.e. $\Delta\lambda/\lambda$ and horizontal divergence for the exploring or incident beam, which are respectively around 10^{-5} and much less than 3 arc s of the multocrystal X-ray diffractometer used in the present studies. The influence of such defects may not influence much on the NLO properties. However, a quantitative analysis of such unavoidable defects is of great importance, particularly in case of phase matching applications [12].

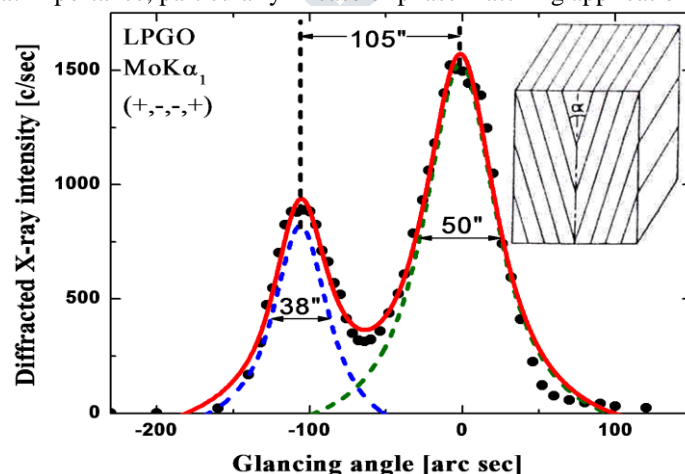


Fig 2: Diffraction curve recorded for a typical LPGO single crystal using (010) diffracting planes with $MoK\alpha_1$ radiation. Inset shows the schematic of a structural grain boundary

3.3. SINGLE CRYSTAL XRD ANALYSIS

Single crystal XRD analysis for the grown LPGO crystal is carried out using Bruker Kappa Apex-II X-ray diffractometer. The determined lattice parameter values are $a = 10.57 \text{ \AA}$, $b = 5.69 \text{ \AA}$, $c = 12.09 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 113.83$ and $V = 659 \text{ \AA}^3$. From the results, it is observed that LPGO crystallizes in the monoclinic structure with a space group $P2_1/c$, which is in good agreement with the reported values [7]. As compared to pure glycinium oxalate crystal, very slight change in the lattice parameters and cell volume of L-proline doped glycinium oxalate (LPGO) compound is observed from the single crystal XRD analysis, which can be attributed to the lattice distortion by dopant in the parent compound.

3.4. FTIR ANALYSIS

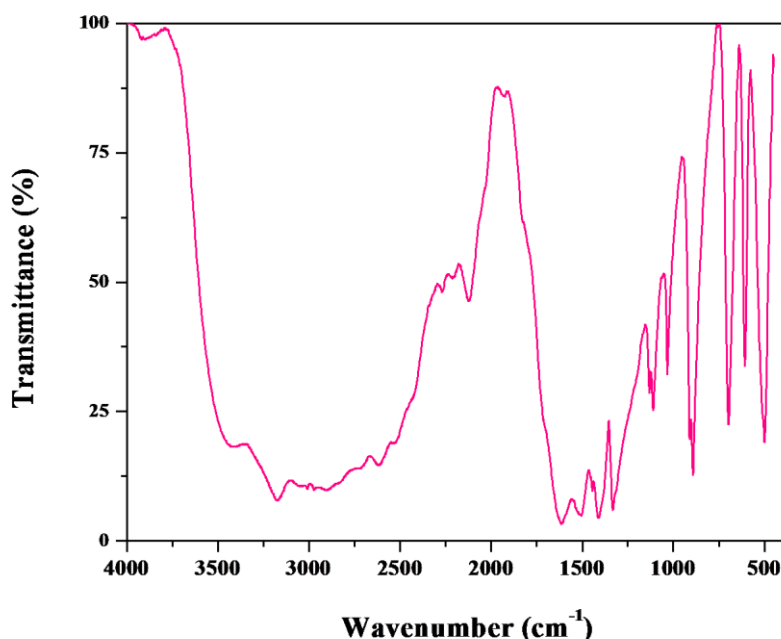


Fig 3: FTIR spectrum of LPGO single crystal

The FTIR spectra of the LPGO grown crystals are recorded using KBr pellet technique in the region 4000 to 400 cm^{-1} using a Bruker Model IFS 66V spectrometer. Fig.3 shows the FTIR spectrum of LPGO crystal. In the high-energy region of the spectrum, there is a broad-like envelope between 2628 and 3328 cm^{-1} resulting from the hydrogen bonded symmetric and asymmetric stretching vibrations of NH_3^+ group [13]. The peaks at 2733 and 3174 cm^{-1} correspond to asymmetric and symmetric stretching vibration of COO^- . The peaks at 2628 and 1332 cm^{-1} are attributed to CH stretching vibration and CH_2 wagging, respectively. Further, a strong band located at 882 cm^{-1} is attributed to the bending modes of C-H and CH_2 groups of L-Proline [14]. In addition, the bands observed at 605 and 698 cm^{-1} are attributed to carboxylate groups while the absorption peak at 1111 cm^{-1} is attributed to NH_3^+ group. Thus, carboxyl group is present as carboxylate ion and amino group is present as ammonium ion in glycinium oxalate.

3.5. UV TRANSMISSION STUDIES

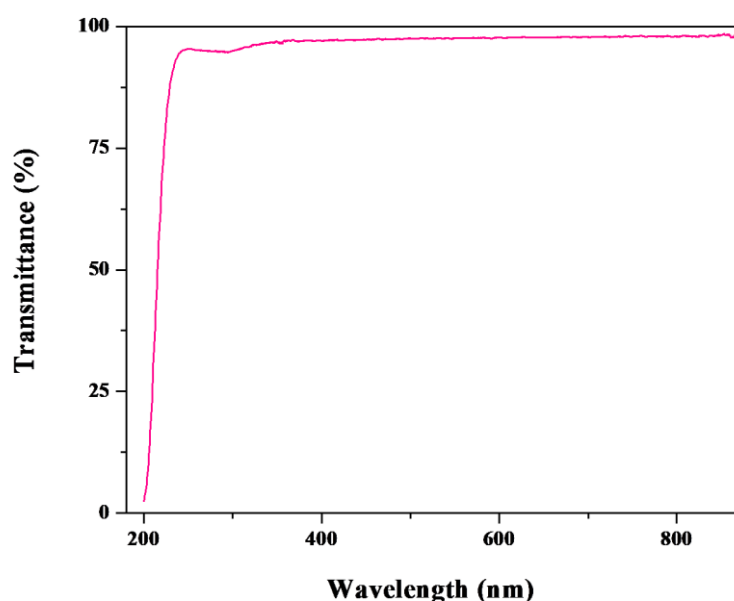


Fig 4: UV-visible spectrum of LPGO crystal

The UV-vis transmission spectrum of LPGO sample in the range of 200-1000 nm is recorded by using a Varian Cary 5E spectrophotometer as shown in Fig.4. It is cleared that the crystal has a transparency window from 202 to 839 nm, which makes it

a very potential material for blue light emission [15]. From the spectrum, it is observed that the LPGO crystal has a lower cut-off wavelength of 244 nm and their corresponding band gap energy (E_g) value of the LPGO crystal is calculated to be 5.08 eV. It is observed that there is no significant absorption in the visible and infrared spectral regions and it indicates the better optical quality of LPGO single crystal [16].

4. CONCLUSIONS

Single crystals of LPGO have been successfully grown by slow evaporation solvent method. The crystalline perfection is assessed by HRXRD and found to be fairly good. The monoclinic crystal structure of LPGO is determined from single crystal XRD analysis. The presence of various functional groups of LPGO is identified from the FTIR analysis. The UV-visible-NIR spectrum of LPGO shows that there is no absorption in the entire visible region. The wide transmission range in the entire visible region enables it to be a potential candidate for optoelectronic applications.

ACKNOWLEDGEMENT

The authors are grateful to Dr. G. Bhagavannarayana, National Physical Laboratory (CSIR), Dr. K.S. Krishnan Road, New Delhi 110 012, India, for the assistance of HR-XRD analysis.

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