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Research Paper

Optical Studies of Glycine Phosphite (GPI) Single Crystals for Optical Devices

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Glycine Phosphite (GPI) a ferroelectric type crystal was grown in aqueous solution by conventional solution growth technique. Powder X-ray diffraction studies indicate the monoclinic structure of GPI crystal and FTIR study confirms the chemical components present in the grown crystal. The optical transparency and cutoff wavelength of the grown crystal was examined by UV-Visible spectral studies. The optical parameters such as optical band gap, absorption coefficient, extinction coefficient and refractive index of the grown GPI crystals were calculated for optical device applications.

Key Words: Growth from Solution; X-ray Diffraction; Optical Band Gap; Absorption; Coefficient; Refractive Index

Introduction

Ferroelectric materials are preferred in a wide variety of electronic and optical devices due to their marked dielectric, piezoelectric and pyroelectric properties. Glycine, a simple amino acid easily forms crystals with selected inorganic and organic species. In this aspect, Glycine Phosphite (GPI) is identified as a good ferroelectric material. Its strong piezoelectric and pyroelectric properties were reported by several researchers [1-5]. The detailed investigation of optical parameters are required to fabricate materials for specific applications such as optoelectronic devices [6, 7]. The knowledge of optical constants of the materials such as optical band gap and extinction coefficient is quite essential to examine the atomic structure, electronic band structure and electrical properties. The refractive index renders the details about the chemical bonding and electronic structure of the material. An accurate measurement of the optical parameters can be easily performed on semiorganic crystals [8]. In the present work, the material synthesis, crystal growth, structural and FTIR studies and optical constants estimation of GPI crystal through optical spectral studies were reported.

Experiment

Synthesis and Crystal Growth of GPI

GPI was synthesized by dissolving glycine and phosphorous acid in the stoichiometric ratio of 1:1 using deionised water as a solvent. The glycine phosphite material was synthesized according to the following reaction,

$$NH_2CH_2COOH + H_3PO_3 \rightarrow (NH_3CH_2COOH).H_2PO_3.$$

After the complete dissolution of these compounds, the solution was cooled below room temperature by refrigeration. The synthesized salt was further purified by three times recrystallization process.

Based on the calculated solubility data 33 g/100 ml at 30ºC [9], the growth solution was saturated. The prepared solution was filtered and covered with

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a perforated polythene sheet to restrict the fast evaporation of the solvent. The prepared solution was kept in a constant temperature bath (of accuracy ±0.01ºC) at 40ºC to grow bulk crystals by slow evaporation.

A good quality transparent single crystal with regular shape and size of 14 x 12 x 2 mm^3 was grown from mother solution within 25 days. Large sized, defect free, high transparency GPI crystals can be grown by SR method [10, 11]. The photograph of as-grown crystal of GPI is shown in Fig. 1.

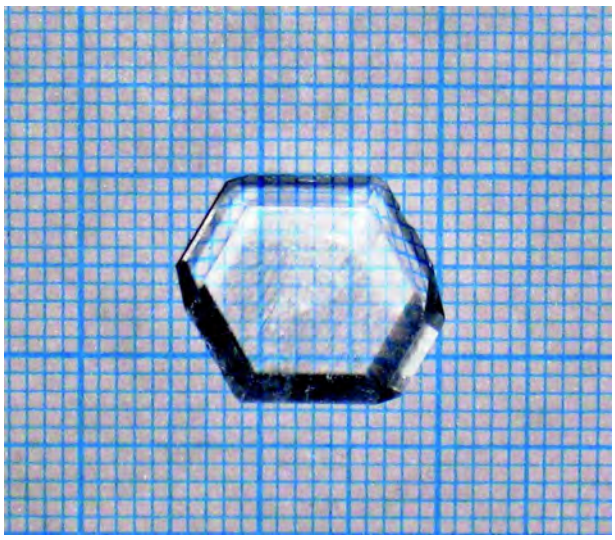

Fig. 1: Photograph of as-grown GPI crystal

Results and Discussion

X-ray Diffraction Analysis

The grown GPI crystal was subjected to powder X-ray diffraction analysis, using a Bruker D8 ADVANCE diffractometer with CuKα (λ = 1.54187 Å) radiation. The powder pattern was recorded in the range of angle from 10º to 60º with a Cu target and Ni filter at 40 kV and 30 mA with the scanning speed of 0.021/s. The observed powder XRD pattern of GPI is shown in Fig. 2. All the peaks were indexed and lattice parameters values were calculated (Table 1). It is observed that these values are in good agreement with the reported values [12]. From this study, it was confirmed that GPI crystallized in the monoclinic system with the space group of $P2_1/a$.

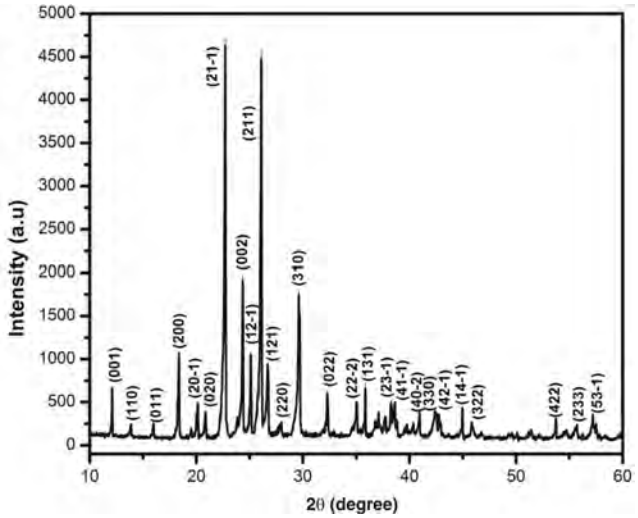

Fig. 2: Powder XRD pattern of GPI

FTIR Spectral Analysis

Fourier transform infrared spectrum of GPI crystal was recorded in the range 4000-400 cm^{-1} with a Nicolet Avator 330A Spectrophotometer by KBr pellet technique. This provides the sufficient information about the structure of GPI compound as shown in Fig. 3. The vibration modes of various functional groups of GPI material and their respective frequencies are tabulated (Table 2). These observed frequencies are found to be in good agreement with the reported values [13, 14].

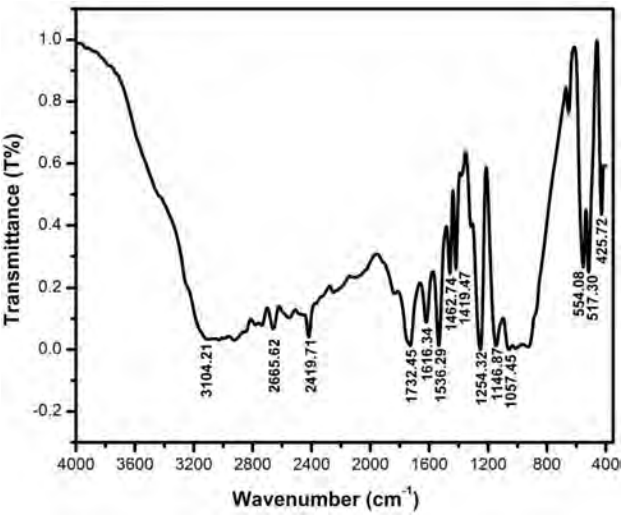

Fig. 3: FTIR spectrum of GPI

Table 1: The estimated lattice parameter values of GPI single crystal

Lattice parameters	Reported [12]	Present work
a (Å)	9.793	9.836
b (Å)	8.481	8.526
c (Å)	7.409	7.440
β (°)	100.430	100.360

Table 2: FTIR spectral vibration mode assignments of GPI crystal

Wavenumber (cm^{-1})	Assignments
3104.21	NH_3 asymmetric stretching
2665.62	NH_3 symmetric stretching
2419.71	P-H stretching
1732.45	C=O stretching
1616.34	N-H bend Asymmetric mode
1536.29	N-H bend Symmetric mode
1462.74	CH_2 bending
1419.47	COO^- stretching and CH_2 scissoring
1254.32	C-O stretching
1146.87	PO_2 asymmetric stretching
1057.45	P=O symmetric stretching
554.08	COOH wagging
517.30	NH_3^+ rocking
425.72	PO_3 symmetric bending

Optical Absorption Studies

The UV-Visible optical absorption spectrum of as grown GPI crystal was recorded in the wavelength region ranging from 200-1100 nm using Perkin-Elmer Lambda 35 Spectrophotometer and is shown in Fig. 4. For optical device fabrication, the crystal should be transparent in the considerable region of wavelength [15, 16]. GPI crystal is transparent in the entire visible region and has cutoff wavelength around 250 nm

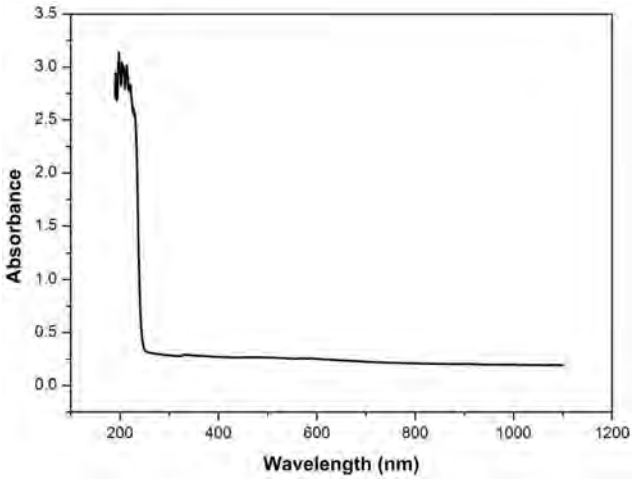

Fig. 4: Optical absorption spectrum of GPI

which makes it as a potential material for optical device fabrication. The transparency of GPI can be improved by SR method [10]. The enhancement in the percentage of transmission by SR method may be attributed to a reduced scattering from structural and crystallographic defects like point defects, line defects, low angle boundaries, vacancies or voids. Hence higher transmittance in SR grown GPI shows that the defect concentration in the grown crystal is less.

The optical absorption coefficient (α) was calculated using the relation

$$\alpha = \frac{2.3026 \log(1/T)}{t} \quad (1)$$

where, T is the transmittance and t is the thickness of the crystal.

The optical band gap (E_g) has been evaluated from the transmission spectrum and the optical absorption coefficient (α) can be calculated by the equation [17],

$$h\upsilon\alpha = A(h\upsilon - E_g)^{1/2} \quad (2)$$

where A is a constant, the direct optical band gap, h the Plank's constant and n the frequency of the incident photons.

The band gap of GPI crystal was estimated by

plotting $(\alpha h\nu)^2$ vs. $h\nu$ as shown in Fig. 5 and the band gap energy was found to be 5.17 eV. As a result of wide band gap, the grown crystal has large transmittance in the visible region [18].

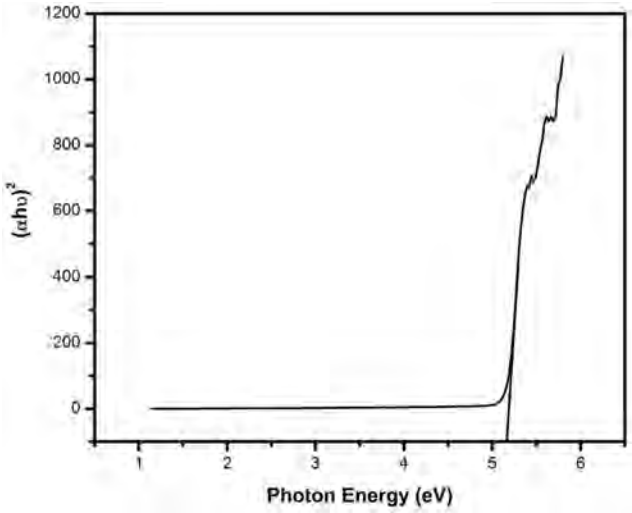

Fig. 5: Optical band gap energy (Eg) of GPI

Evaluation of Optical Constants

The extinction (K) related to the absorption is given by [19].

$$K = \frac{\lambda\alpha}{4\pi} \tag{3}$$

Reflectance (R) in terms of the absorption was obtained and is given by

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \tag{4}$$

The refractive index (n) was determined from the reflectance (R) data using the relation [20].

$$n = \frac{-(R+1) \pm 2\sqrt{R}}{(R-1)} \tag{5}$$

From the recorded UV-VIS-NIR transmittance spectrum, the linear optical constants of GPI were calculated and the variation of optical constants (K, n) as a function of photon energy and wavelength are plotted in the Figs. 6 and 7. From these plots, it is known that the refractive index decreases with the increase of wavelength. The high transmission, low extinction coefficient and low refractive index of crystals in the UV-VIS region makes the GPI material a prominent one for antireflection coating in solar thermal devices.

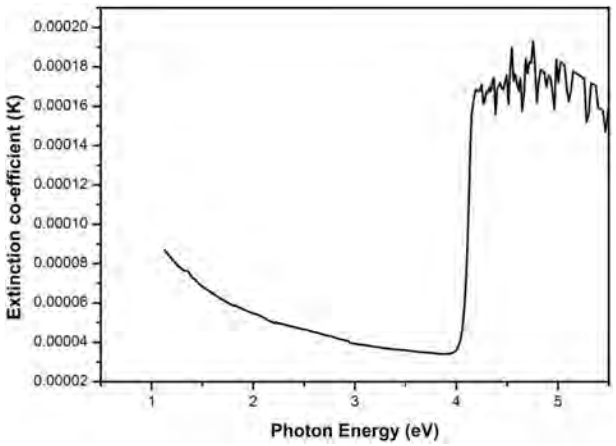

Fig. 6: Extinction coefficient (k) *vs*. photon energy

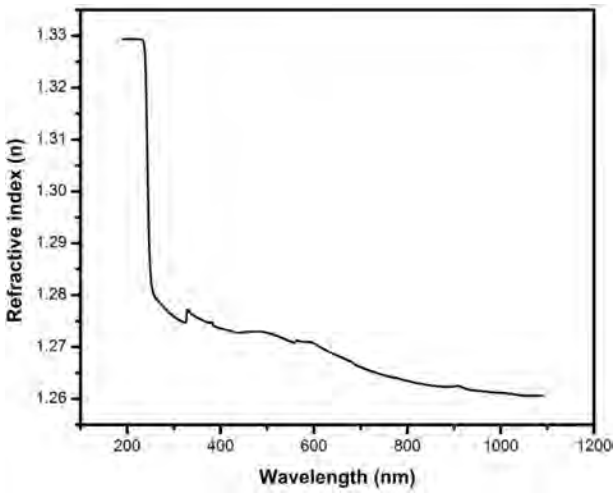

Fig. 7: Refractive index (n) *vs*. wavelength

Conclusion

Large size single crystal of GPI was successfully grown by slow evaporation technique. Monoclinic crystal structure and lattice parameters of the grown

crystals were confirmed by powder X-ray analysis. The presence of phosphorous acid with the glycine was confirmed and functional groups of GPI were identified through FTIR spectral studies. Optical studies reveal that the grown crystal has low cutoff wavelength with wide optical window and the band gap energy for the grown crystal was found to be 5.17 eV. The optical constants, extinction coefficient (K) and refractive index (n) indicates the high transparency of the crystal and confirms its suitability for optical device fabrication.

References

1. Dacko S, Czapla Z, Baran J and Drozd M *Phys Lett* **A 223** (1996) 217
2. Tritt-Goc J, Pislewski N, Szczepanska L and Goc R *Solid State Comm* **108** (1998) 189
3. Tchukvinskyi R, Cach R, Czapla Z and Dacko S *Phys Stat Sol* (a) **165** (1998) 309
4. Balashova EV, Lemanow VV and Pankova GA *Phys Solid State* **47** (2005) 183
5. Balashova EV and Lemanov VV *Ferroelectrics* **285** (2003) 179
6. Bredas JL, Adant C, Tackx P and Persoons A *Chem Rev* **94** (1994) 243
7. Metha PV, Tripathi N and Kumar SK *Chalcogenide Lett* **2** (2005) 39
8. Dongol M *Egypt J Sol* **25** (2002) 33
9. Deepthy A and Bhat HL *J Cryst Growth* **226** (2001) 287
10. Senthil Pandian M, Pattanaboonmee N, Ramasamy P and Manyum P *J Cryst Growth* **314** (2011) 207
11. Supriya S, Kalainathan S and Bhagavannarayana G *J Phys Chem Solids* **74** (2013) 70
12. Baran J, Lukaszewicz K, Pietraszko A and Sledz M *J Mol Struct* **611** (2002) 155
13. Renuka K, Devi and Srinivasan K *Cryst Res Technol* **46** (2011) 1265
14. Perumal R, Senthil Kumar K, Moorthy Babu S and Bhagavannarayana G *J Alloys Comp* **490** (2010) 342
15. Krishnakumar V and Nagalakshmi R *Spectro Chim Acta* **A 61** (2005) 499
16. Krishnakumar V and John Xavier R *Spectro Chim Acta* **A 60** (2005) 709
17. Watanabe I and Okumura T *Jpn J Appl Phys* **25** (1986) 1851
18. Eya DDO, Ekpunobi AJ and Okeke CE *Acad Open Internet J* (2006) 17
19. Pankove J I *Optical Processes in Semiconductors* Prentice Hall New York (1971)
20. Dhanaraj PV, Suthan T and Rajesh NP *Curr Appl Phys* **10** (2010) 1349.