Growth, Structure and Optical Studies of Undoped And Potassium Nitrate Doped Glycine Single Crystals

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Abstract

Single crystals of undoped and potassium nitrate doped glycine were grown by slow evaporation technique at room temperature after repeated recrystallization process. The vibrational frequencies of various functional groups present in the grown crystals have been derived from the FTIR analysis in the range of 400 to4000cm^{-1}.The range and percentage of optical transmission are ascertained by recording UV-Vis spectrum. Powder X-ray diffraction patterns were recorded and the hkl values for corresponding 2 theta values were indexed for the structural conformation. It proves the presence of both the parent materials in the grown crystal. Vickers micro hardness test was carried out to analyse the mechanical property of the grown crystals which helps us to conclude about the hardness nature of the crystals.

Keywords: Slow Evaporation, FT-IR, Powder X-Ray Diffraction, Micro Hardness Test.

Introduction

In recent years, organo-inorganic hybrid materials have attracted considerable attention [1]. The most popular nonlinear optical [NLO] materials used to produce second harmonic generation[SHG] signal so far have been inorganic bulk crystals with rather small [SHG] susceptibilities, such as potassium dihydrogen phosphate (KDP) [2]. But due its lower SHG efficiency and laser damage threshold, materials scientist focused their attention on organic materials because they posses' large [SHG] susceptibilities due to delocalized π-electrons.

Inorganic materials are much more mature in their application to NLO than the organic materials. The large nonlinearity in organic materials arises from the strong charge transfer and high polarizability. In particular, the inorganic derivatives of protein amino acids are often attributed to symmetric groups without an inversion centre mostly to polar symmetry groups. One major difference between inorganic and organic crystals is that only relatively weak Vander walls forces are hydrogen bonding, resulting in rather poor mechanical properties often couples the molecules in pure organic crystals. Hence the molecules being held together by comparatively weak dispersive forces, the molecular identity in organic crystal is preserved. Accordingly, the molecular absorption will control the absorption spectrum of the crystal. Hence, organic materials are perceived as being structurally more diverse and are believed to have more long-term promise than inorganic [3]. Glycine (NH_2CH_2COOH: amino acetic acid), the simplest amino acid, has no centre of chirality and is optically inactive. The γ-glycine crystallizes in non-centrosymmetric space group $P3_1$, making it a potential candidate for Piezoelectric and NLO applications [4]. In the present study, we report the growth and characterization studies of γ-glycine crystals grown from aqueous solution of γ-glycine in the presence of Potassium Nitrate for the first time, since some of the physical properties of the reported γ-glycine crystals are enhanced by this solvent.

Materials and Methods

AR grade (99%) pure salts of Potassium Nitrate and γ-glycine were used in the preparation of single crystals of γ-glycine and Potassium Nitrate doped Glycine (PNG). Saturated solutions of glycine and potassium nitrate were prepared using deionised water at room temperature using magnetic stirrer. Both the solutions were doubly filtered using Whatman No.1 filter paper. The prepared saturated solution of glycine is taken in one beaker. In another beaker, the saturated solutions of KNO_3 and glycine were mixed in the ratio 1:1. The solutions in the above two beakers were stirred for 5 hours to get a clear and homogeneous medium. The beakers are covered with perforated aluminium foil and kept in an undisturbed location for the growth of crystals. After 7 and 67 days, good quality, transparent and colourless single crystals of glycine and PNG were obtained. The harvested crystals were recrystallized repeatedly to improve the quality. The photograph of the grown PNG crystal of dimension $5x3x2mm^3$ is shown in fig.1. The grown crystals were characterized using different techniques like PXRD, FTIR, UV-Vis and microhardness analysis.

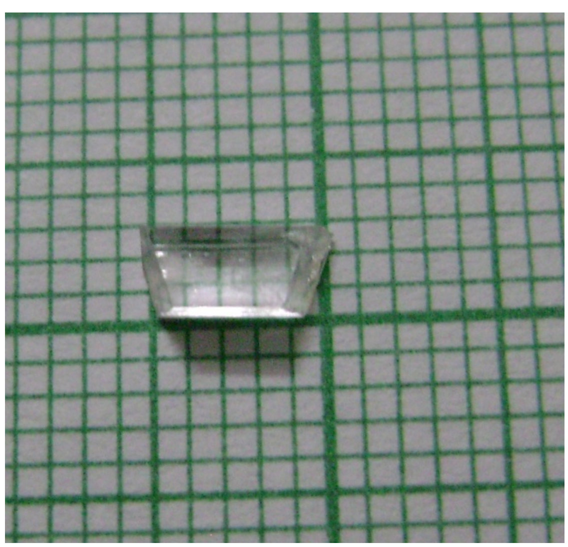

Fig.1. Grown single crystal of PNG

Characterization

Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction pattern was recorded using a Rich Seifert diffractometer with Cu Kα (λ=1.5418 Å) radiation by crushing the glycine and PNG single crystals into fine powder to demonstrate the crystalline nature of title compound. The sample was scanned over the range 10 - 90° at the rate of 1° per minute. The indexed PXRD pattern of the grown crystal is shown in fig.2. The sharp peaks indicate the crystalline nature of the grown crystals. All the reflections were indexed using JCPDS software.

From figure.1 it is clear that the doped crystal consists of additional peaks other than that of glycine which confirms the possibility of modification of glycine structure.

FTIR Spectrum analysis

FTIR spectroscopy can be used to identify compounds or investigate sample composition. FT-IR spectrum of the grown crystal was identified by the KBr pellet technique using a Perkin Elmer FT-IR spectrometer in the range 4000–400cm^{-1}. The recorded FTIR spectrum is shown in the Fig.3 and band assignment are given in table 1. C=O is represented by the peak at 1641 cm^{-1}. The peak at 1539 cm^{-1} is due to presence of NH_2^+. The presence of carboxyl group is confirmed by 1370 and 501cm^{-1}. The peak at 829 cm^{-1} is due to NO group bending. N-H bending is confirmed by the peak at 422 cm^{-1} [5].

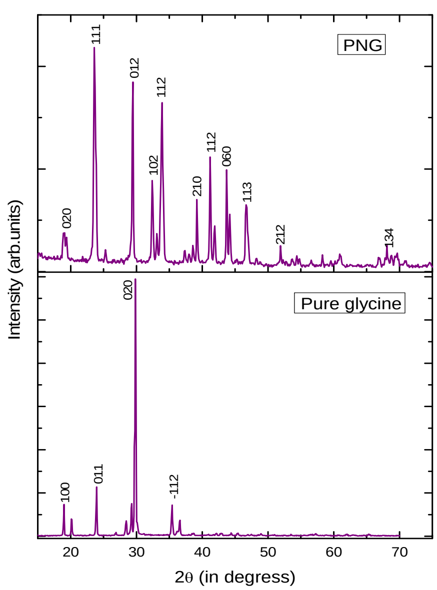

Fig.2 PXRD pattern of the grown crystal

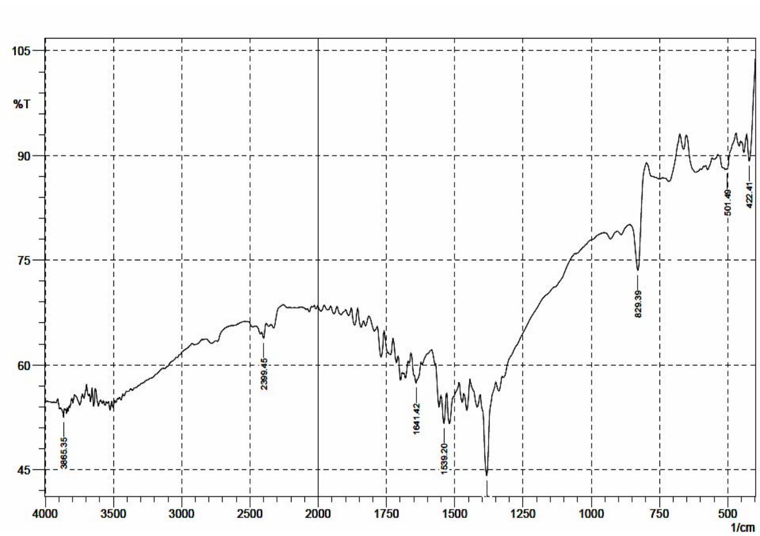

Fig.3. FTIR Spectrum of the grown crysta

Table.1. FTIR data table of PNG single crystals

Wave number (cm^{-1})	Band Assignment
1641	C=O stretching
1539	Absorption due to NH_2^+
1370,501	Carboxyl group
829	NO group bending
422	N-H bending

UV-Visible Spectroscopy

To know the suitability of the grown single crystals for optical applications [6-7], the optical transmission spectrum of the grown PNG crystals was recorded in the wavelength range 200 to 800 nm using a Perkin Elmer lambda 35 UV-Vis spectrometer. The recorded spectrum is shown in the Fig.4.

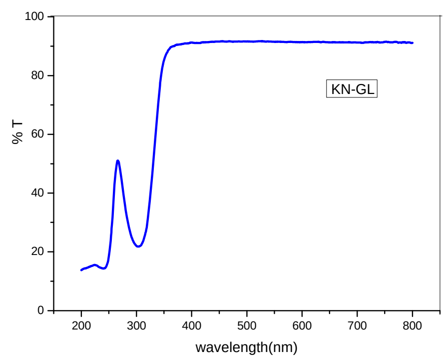

Fig.4. UV-Vis spectrum of grown crystal

The lower cut-off wave length is around 366 nm and band gap is 3.39eV. The transmittance of the crystal is found to be 90% in the entire visible region. This quality of the grown crystal makes it suitable for NLO applications.

Microhardness Study

Mechanical strength of the materials plays a key role in device fabrication [8]. Micro hardness measurements were carried out by Vickers's hardness test at room temperature. The hardness measurements were taken for applied load varying from 25 to 100gm. The Vickers hardness number (H) was calculated using the relation

$$H_v = \frac{1.8544\,P}{d^2}\,\frac{kg}{mm^2}$$

where, P-is the applied load, d-is the diagonal length of the indentation impression. The variation of H_v with the applied load P is shown in fig.5. It is evident from the plot that the hardness number of the grown crystal increases with the applied load.

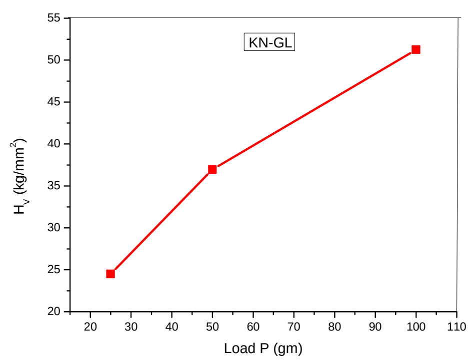

Fig.5.The variation of H_v Vs load

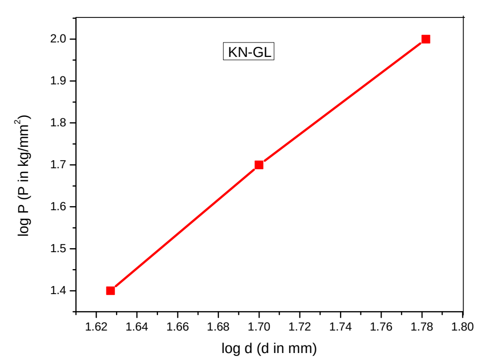

Fig.6. plot between log P Vs log d

A plot between log P Vs log d for the grown crystal is shown in fig.6. This plot yields a straight line graph, and its slope gives the work hardening index n which is found to be greater than 1.6 which proves that grown crystal belongs to soft material [9-10].

Conclusion

Single crystals of Potassium Nitrate doped and undoped glycine were successfully developed using slow evaporation technique. Crystalline nature of developed crystals was verified with PXRD analysis and reflections were duly indexed. Various functional groups present in the crystals were identified through FTIR analysis. Optical behaviour of the crystal was analyzed with UV-Visible spectrum which elucidates that lower cut off wave length is around 366nm and band gap energy is 3.39eV. Mechanical part of the analysis says that the grown crystal is a soft material. From the above results, the author suggests that the essential properties of glycine single crystals were enhanced due to the addition of KNO_3 and the grown crystal is suitable for NLO applications.

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