

Crystallization and characterization of nonlinear optical material: Glycolylurea

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Abstract

Glycolylurea an intriguing organic material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. The solubility studies have been carried out in the temperature range 30 - 60°C. Single crystals have been grown by slow evaporation method from deionised water. These crystals were characterized by FTIR, UV-Vis and Hardness studies. The crystal belongs to monoclinic with space group $C_2/c1$. FTIR spectral studies were performed for conformation of the Glycolylurea molecule and hydrogen bonds. The optical transmission spectra of the grown crystal are tested by UV – vis spectrophotometer and found that the crystal was transparent over entire visible region. The mechanical response of the crystal has been studied using Vickers microhardness technique.

Keywords: Crystal Growth, FTIR studies, UV-Vis studies, Hardness studies

Introduction

The design and synthesis of the required efficient π - electron donors constitutes an active area of modern materials chemistry. Second order nonlinear optical materials have attracted much attention because of potential utilization in photonic applications. The added esteem of nonlinear optical materials [1-3] over lasers and electro optics became preponderant from the early days of lasers. The advantage of organic materials is that they can be optimized at the molecular engineering level for a specific application. Different engineering guidelines lead to different organic materials optimized for photorefractivity, holographic memory, or electro-optic modulation [4]. Also within a chosen application, the chromophore can still be optimized for the specific wavelength used. Another advantage of organic materials is that they combine chemical functionality with their optical properties. Apart from exhibiting nonlinear optical properties, with the inherent charge electron transfer properties between donor and acceptor groups, one of these groups can in addition have redox or proton-transfer capability. Studying the effect of inter- and intra-molecular processes directly or indirectly involved in nonlinear optical processes will be helpful to design novel crystals for the next generation of nonlinear optical devices. Glycolylurea also qualifies for electrooptic applications. In this work, Glycolylurea crystals were grown and subjected to various characterizations.

Solubility and Crystal Growth

The low-temperature solution growth technique is widely used for the growth of organic and inorganic single crystals to get more transparent single crystals. The commercially available Glycolylurea ($C_3H_4N_2O_2$) is purified by repeated recrystallization process. The

repeated recrystallized materials have been used for growth as charge material. Since Glycolylurea is soluble in deionised water, we have chosen deionised water as solvent for our growth. The growth process and the quality of crystals significantly depend on supersaturation. The saturated solution of Glycolylurea was obtained by dissolving the charge material into the solvent with continuous stirring of the solution using a magnetic stirrer at room temperature (32°C). On reaching saturation, the equilibrium concentration of the solute was determined by gravimetry. The beaker containing the solution was optimally closed for controlled evaporation. Bright white transparent single crystals were obtained from the mother solution after a week. Fig. 1 shows the Solubility curve of Glycolylurea. Fig. 2 shows the grown crystal of Glycolylurea with an optimized solution pH value of 3.5.

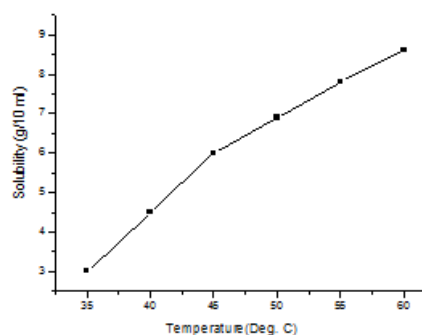


Fig. 1 Solubility curve of Glycolylurea

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Fig. 2 Grown crystal of Glycolylurea

Powder X-ray diffraction studies

From the powdered X-ray data, it is found that the structure of the grown crystal is monoclinic with space group $C_2/c1$. The lattice parameter values of the crystal have been calculated using least-squares fit method and they are found to be $a = 9.4238 \text{ \AA}$, $b = 12.5722 \text{ \AA}$, $c = 7.1786 \text{ \AA}$ making an angle $\alpha = \gamma$ of 90° and $\beta = 104.343$. The XRD patterns obtained in the present study are essentially identical with literature. It reveals the excellent crystallinity of the grown material. From the studies Fig. 3 represents the chemical structure of the grown material.

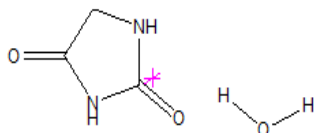


Fig. 3 Chemical structure of Glycolylurea.

FTIR Measurements

The room temperature Fourier transform infrared spectrum of Glycolylurea was recorded in the region $400\text{--}4000 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} using Perkin Elmer Fourier transform Infrared Spectrophotometer, model SPECTRUM RX1, using KBr pellets containing a fine Glycolylurea powder obtained from the grown single crystals. The measured FTIR spectrum is presented in Fig. 4.

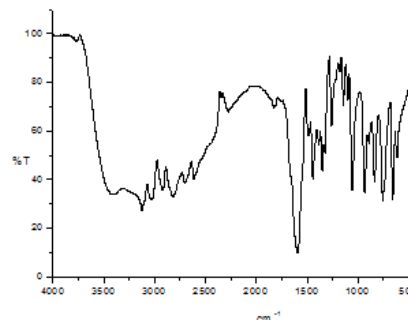


Fig. 4. FTIR spectrum of Glycolylurea.

The present vibrational spectroscopic study was carried out with a view of obtaining an insight into the structural aspects of optical nonlinearity of crystals. In order to understand the existence of bonding nature the present study has been undertaken. Thus the molecular structure of the synthesized compound was confirmed by the spectral analysis. The observed wavenumbers, relative intensities obtained from the recorded spectra and the assignments [5-7] proposed for the title nonlinear optical crystal is given in Table. 1. The assignments of bands observed in the vibrational spectrum are an essential step for solving structural and chemical problem.

Table. 1. Observed IR wavenumber of Glycolylurea and its vibrational assignments.

FTIR Observed wavenumber cm^{-1}	Assignments
3407	N-H Stretching
3124	C-H Stretching
3032	C-H Stretching
2612	C-H Stretching in CH_2 group
2344	C-H Stretching in CH_2 group
2123	C-H Stretching in CH_2 group
1594	C=O Stretching
1486	C=O Stretching
1409	C-N Stretching
1350	C-N Stretching
1101	Ring breathing
1055	Ring vibrational
892	N-H ipb
657	C=O ipb
615	N-H opb
503	C=O opb

Optical Measurements

The optical transmittance plays an important role in identifying the potential of the NLO material. Because the material can be of utility if it has wide transparency window with reduced absorption around the fundamental and second harmonic wavelength. The lower cutoff wavelength lies around 250 nm which is due to the $\pi\text{-}\pi^*$ transition in this compound. In this crystal the UV transmittance ranges from $200\text{--}1100 \text{ nm}$, which is very important for the realization of SHG output. In order to determine the transmission range and

hence to know the suitability of single crystal for optical applications, the UV-Vis transmittance has been performed using Perkin Elmer Lambda 35 UV visible spectrophotometer and the transmittance spectrum is shown in Fig. 5. From the results of UV-Visible spectral data, it can be expended as a potential material for SHG in the visible region down to blue and violet light, which makes it suitable for opto electronic application. The reduction in absorption around Nd: YAG laser fundamental wavelength contributes the resistance of the material to laser damage threshold. The step decrease in

transmittance around 250nm may be assigned to electronic excitation in COO- group. As there is no change in transmittance in the entire visible range from 250nm the materials can find application as window in spectral instruments in those region.

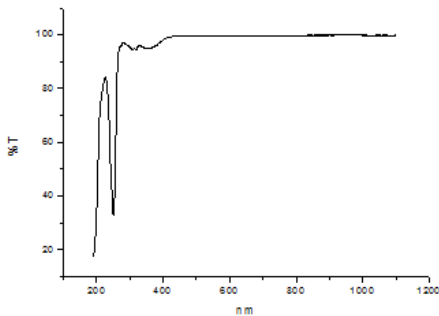


Fig. 5 Optical transmission spectra of Glycolylurea

Hardness studies

One of the important properties of any device material is its mechanical strength, represented by its hardness. Physically hardness is the resistance offered by a material to localized plastic deformation (moment of dislocations) caused by scratching or by indentation. This resistance is the intrinsic property of the crystal. The hardness is generally measured as the ratio of applied load to the surface area of the indentation. Indentation hardness measurement can, in principle, be carried out at fairly high loads (~100 Kg). But for materials which have low hardness and which are available as small-sized sample, it is convenient to make measurements at low loads of < 200g. The low load hardness is called microhardness. The grown crystal with smooth and dominant face was selected for microhardness studies. Indentations were carried out using Vickers indenter for varying loads (25-200 g), for each load, several indentations were made and the average value of diagonal length was used to calculate the microhardness. In ideal circumstances, measured hardness values should be independent of the applied load. But in practice, load dependence is observed. Vickers microhardness number was determined using $H_v = 1.8544 P/d^2$ Kg/mm². The hardness number was found to increase with the load upto 200g and after a load of 200g cracks developed in the material. This may be due to the release of internal stresses generated locally by indentation. The plot drawn between the corresponding loads and hardness values of the Glycolylurea is shown in Fig. 5.

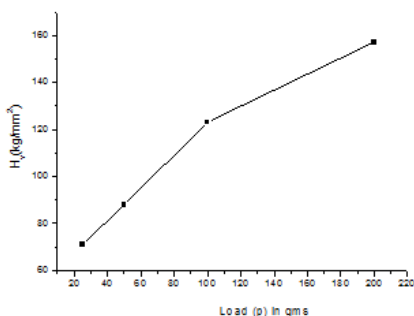


Fig. 5. Mechanical behaviour of Glycolylurea

Nonlinear Optical studies

A quantitative measurement of the conversion efficiency of

Glycolylurea was determined by the modified version of powder technique developed by Kurtz and Perry [11-12]. The non-zero measured powder SHG signal is reliable with the SHG activity, which can be correlated with noncentrosymmetric crystal structure. The relative efficiency of Glycolylurea with that of KDP has been measured. It is found that the efficiency of the title crystal (142 mV), which is 15 times greater than that of KDP (9 mV). The result of SHG is also supporting for further studies.

Conclusion

Good optical quality Glycolylurea single crystals were grown by solution growth method at room temperature. It is a promising candidate for NLO applications. The lattice parameters were found by Powdered XRD technique. The FTIR spectrum reveals that the confirmation of the molecular structure of the grown specimen. From the results of optical transmission it was found that the crystal exhibit excellent transmission in entire UV-Vis range studied. This property enables the material for the fabrication of IR detectors and in some optoelectronics device technology. The mechanical properties were examined and from the results it is found to be significant effect on machining the crystal for device purpose.

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