



Growth and optical properties of diglycine hydrobromide

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ABSTRACT

Diglycine hydrobromide an intriguing material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. Their structural, optical and physicochemical properties were characterized by X-ray powder diffraction and UV-Vis spectra. The title crystal has found to crystallize into noncentrosymmetric orthorhombic P_{212121} space group. The material has a wide transparency in the entire visible region. It is found that the cutoff wavelength lies in the UV region. The dielectric studies were carried out using the instrument, N4L LCR meter. The compound is a prospective crystalline material for second order nonlinear optical application.

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Introduction

The development of functional molecular materials with desirable physical properties such as ferroelectric, ferromagnetic, photo conducting and nonlinear optical (NLO) properties for practical applications has become one of the fast growing multi-disciplinary research areas. In addition to the specific functionalities that a molecule needs to possess, the constituent molecules usually require a certain well defined molecular orientation and arrangement in the solid state so that the corresponding physical properties can be used in the bulk [1-10]. For example, the optical nonlinearity of organic materials is primarily derived from the molecular structure. The expression of the nonlinearity is highly dependent on the geometrical arrangement of the molecules in the condensed medium in the case of second-order NLO processes, but much less so for third-order nonlinearities [11-26]. One can define microscopic nonlinear coefficients (molecular hyperpolarizabilities) that are the molecular equivalents of bulk nonlinear optical susceptibilities. In fact, the bulk susceptibility can be readily related to the susceptibilities of the constituent molecules. The primary step in optimizing the optical nonlinearities in this class of materials is at the molecular level, which then requires a detailed understanding of the relationship between molecular electronic structure and the nonlinear polarization that can be induced in a molecule. In contrast to inorganics, organic materials possess not only peculiar properties but also diversity in molecular and materials design. The addition of halides (Cl and Br) in forming salts with leads to the centrosymmetric arrangement of molecules in the crystal with certain arrangements of water molecules and thus the χ^2 vanishes while χ^3 is possible. The third-order optical nonlinearity does not require noncentrosymmetric structure. Lack of symmetry control may wider the range of possible structures for third-order NLO applications like third harmonic generation and four-wave mixing. However, electronic and other material requirements for practical applications may be extremely difficult to achieve. Therefore, molecular design, synthesis and characterization of

novel materials are expected to play an important role in the development of NLO materials and represent an active field of research at the interface of modern physics, chemistry and materials science [27-31]. In continuation of the above literature survey, this work reports the synthesis, structural, optical and thermal studies of Diglycine hydrobromide crystals.

Synthesis and Growth of Crystal

Analytical reagent (AR) grade samples of Glycine and bromine along with double distilled water were used for the preparation of Diglycine hydrobromide. The salts were prepared by dissolving in water 2:1 molar ratio and kept for the reaction to take place. The product was then purified by repeated crystallization until optically clear tiny crystals were obtained. Small (seed) crystals were grown from saturated aqueous solution by the free evaporation technique at constant temperature (30 °C). Good quality seed crystals were selected for the growth of large single crystals. Large size single crystals were grown by the slow evaporation method using an optically heated constant temperature bath of control accuracy ± 0.01 °C set at 45 °C. Fig 1 shows the Solubility curves of Diglycine Hydro bromide. Fig. 2 shows the as grown crystal of Diglycine Hydro bromide with an optimized solution pH value of 3.8.

Powder X-Ray Diffraction Studies

The grown crystals were subjected to X-ray powder diffraction (XRD) measurements to confirm the material of the crystals grown.

Powder X-ray diffraction studies were carried out using SEIFERT diffractometer with $\text{CuK}\alpha_1$ ($\lambda = 1.5406$ Å) radiation to identify the lattice parameters. Analysis of the X-ray diffraction peaks was done by the available methods and lattice parameters were determined. The crystallographic data is given in Table 1. The diffraction pattern is shown in Fig. 3. Fig 4 represents the molecular packing of the Diglycine hydrobromide in the unit cell. It reveals the excellent crystallinity of the grown material

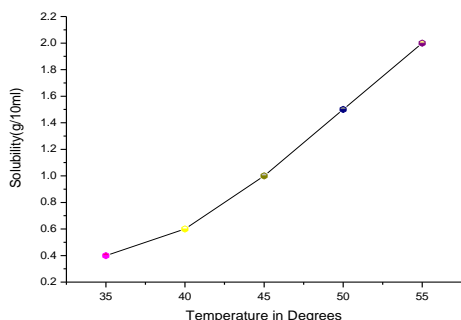


Fig 1. Solubility curves of Diglycine Hydrobromide



Fig 2. Grown crystal of Diglycine Hydrobromide

Table 1. Crystallographic data of Diglycine hydrobromide

Identification code	Diglycine hydrobromide
Empirical formula	C4BrN2O4
Formula weight	219.96
Crystal structure	Orthorombic
Space group	P212121
Cell parameters	
a (Å)	8.21
b (Å)	18.42
c (Å)	5.40
α (°)	90
β (°)	90
γ (°)	90
Volume (Å) ³	816.632
Z	8
Crystal size	12 x 12 x 5 mm ³

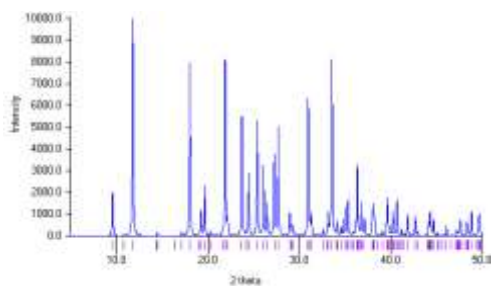


Fig 3. The XRD pattern of Diglycine Hydrobromide

NLO Measurement

NLO test Kurtz SHG test was carried out on Diglycine hydrobromide crystal to study its NLO properties. The sample was illuminated using Q-switched, mode locked Nd:YAG laser with input pulse of 6.2 mJ. The emission of green radiation from the crystal confirmed the second harmonic signal generation in the crystal. The second harmonic signal of 735 mV, were obtained for Diglycine hydrobromide with reference to KDP (275 mV). Thus, the SHG efficiencies of Diglycine hydrobromide crystals are nearly three times greater than KDP[32].

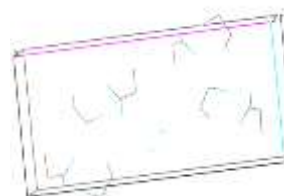


Fig 4. Packing of the Diglycine Hydrobromide in the unit Dielectric Studies

The dielectric study was carried out using the instrument, N4L LCR meter. Samples of known dimension were silver coated on the opposite faces and then placed between the two copper electrodes to form the parallel plate capacitor. The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 2 MHz at room temperature. Figure 5 shows the plot of dielectric constant (ϵ_r) versus applied frequency of the Diglycine hydrobromide crystal. The applied frequency is represented by logarithmic values in the plot. The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency[33-41]. The very high value of ϵ_r at low frequencies may be due to the presence of all the four polarizations namely; space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually[42-46]. The low dielectric loss at high frequency reveals the high optical quality of the crystal with lesser defects, which is the desirable property for NLO applications.

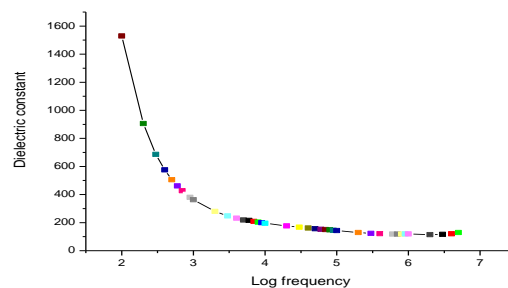


Fig 5 Dielectric behaviour of Diglycine Hydrobromide Optical Transmission Studies

Optical transmittance of Diglycine hydrobromide absorption was studied in the spectral range 190–1100 nm Perkin Elmer Lambda 35 UV visible spectrophotometer. Optically polished single crystal of thickness 2 mm was used for this study. The transmittance spectrum is shown in Fig. 6. It shows good transparency of 55%. The lower cut off of the crystal is found to be 271 nm. After, the fundamental absorption edge a strongly marked shoulder is observed at 378–397 nm, and thereafter the transmission becomes almost constant.

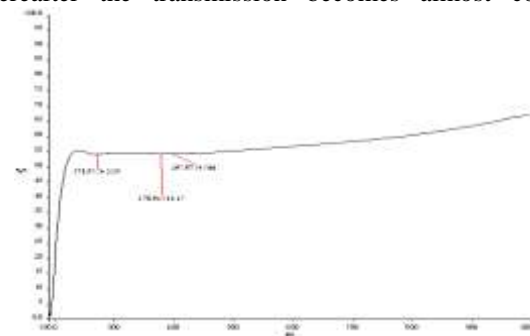


Fig 6. Optical transmission spectra of Diglycine Hydrobromide

Conclusion

Diglycine hydrobromide single crystals were grown by the slow evaporation method from aqueous solutions. The material of the grown crystals was confirmed by XRD studies. The present study indicates that the dielectric parameters, ϵ_r increase at low frequencies. In addition, the results obtained in the present study indicate that the crystal is not only potential NLO materials but also promising low ϵ_r value dielectric materials, expected to be useful in the microelectronics industry.

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