Available online at www.sciencedirect.com
ScienceDirect
Optics Communications 278 (2007) 434–438
OPTICS COMMUNICATIONS
www.elsevier.com/locate/optcom

Growth and characterization of a new organic NLO material: Glycine nitrate

S.A. Martin Britto Dhas, S. Natarajan *

Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Received 7 May 2007; received in revised form 18 June 2007; accepted 19 June 2007

Abstract

Single crystals of glycine nitrate [$(C_2H_6NO_2)^+ \cdot (NO_3)^-$] were grown using submerged seed solution method. The crystals were characterized by using single crystal X-ray diffraction and density measurements. Spectroscopic, thermal and optical studies were carried out for analyzing the presence of the functional groups, thermal stability, decomposition and transparency of the sample. These studies showed that the crystals are thermally stable upto 145 °C and transparent for the fundamental and second harmonic generation of Nd:YAG ($\lambda = 1064$ nm) laser. Second harmonic generation (SHG) conversion efficiency was investigated to explore the NLO characteristics of this material. Microhardness and dielectric studies were also carried out.

PACS: 67.80.Cx; 81.10.h; 81.10.Dn; 61.10.Kw; 65.40.−b

Keywords: Organic compound; Crystal growth; Growth from solution; X-ray diffraction; Thermal properties of crystal

1. Introduction

Organic nonlinear materials will be the key elements for future photonic technologies. Photonics involves the application of photons for information and image processing and is branded to be the technology of the 21st century wherein non-linear optical (NLO) processes have applications such as frequency conversion and optical switching [1]. One of the advantages in working with organic materials is that they allow one to fine-tune the chemical structures and properties for the desired non-linear optical properties [2]. In addition, they have large structural diversity. A number of glycine compounds were reported to possess the NLO property [3–5]. Presently, glycine nitrate (GLN) has been identified as a NLO material. The occurrence of the π–π^* transition in the carboxylic and the nitrate groups accounts for the nonlinearity in this compound. In the present investigation, single crystals of GLN were grown in bulk size and characterized by single crystal X-ray diffraction and density measurements. Fourier transform infrared spectroscopic (FTIR) studies, thermo gravimetric analysis (TGA/DTA), microhardness, UV–Vis–NIR spectral analysis, second harmonic generation (SHG) studies and dielectric studies were also carried out.

2. Experimental

2.1. Crystal growth

Single crystals of glycine nitrate [$(C_2H_6NO_2)^+ \cdot (NO_3)^-$, Fig. 1] were grown from glycine and nitric acid taken in the equimolar ratio in aqueous solution by slow evaporation method. Optically clear and well-shaped crystals were obtained and were used as seed crystals. Bulk crystals were grown from the seeds by using a saturated solution of GLN in a crystallizer, a modified growth apparatus, using submerged seed solution growth method. Transparent crystals

* Corresponding author. Tel.: +91 452 2458471x352; fax: +91 452 2459181.
E-mail address: s_natarajan50@yahoo.com (S. Natarajan).

0030-4018/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.optcom.2007.06.052

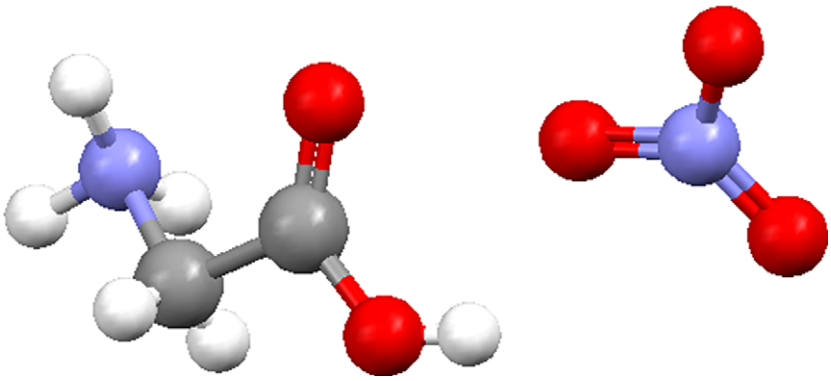

Fig. 1. Molecular structure of glycine nitrate.

of size: $15 \times 11 \times 5$ mm^3 were obtained in a period of about four weeks (Fig. 2).

2.2. Characterization

The grown crystals were subjected to single crystal X-ray diffraction using Nonius CAD-4/MACH 3 Diffractometer, with Mo Kα radiation ($\lambda = 0.71073$ Å). The cell data were obtained from the least-squares refinement of the setting angles of 25 reflections. Density of GLN crystals was determined using the floatation method and had the value of 1.39 kg/m^3. The melting point was found to have the value: 145 (±2) °C. The FTIR spectra of the sample were recorded in KBr phase in the frequency region of 400–4500 cm^{-1} using a Jasco Spectrometer (FTIR, model 410), at a resolution of 4 cm^{-1} and with a scanning speed of 2 mm/s. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out for the crystals, using a NETZSCH-Gerätebau STA 409 PC thermal analyzer. A powder sample was used for the analysis in the temperature range of 26–800 °C with a heating rate of 10 °C/min. The crucible used was of alumina (Al_2O_3), which served as a reference for the sample.

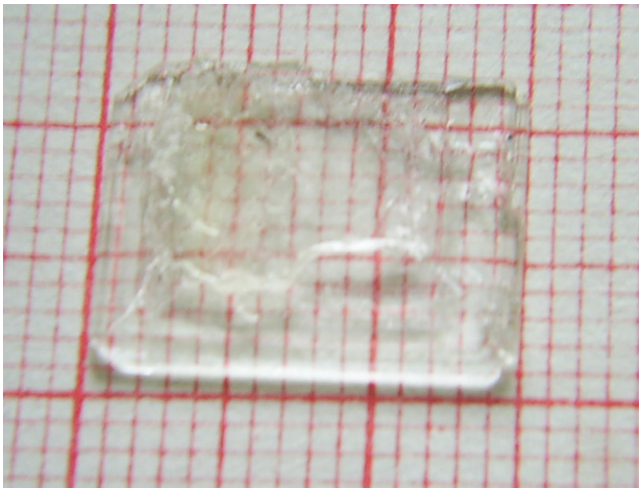

Fig. 2. Glycine nitrate crystal.

The microhardness of the grown crystals was measured using a Siadzu Microhardness Tester (Model No. HMV2T) with diamond indenter. The well polished crystal was mounted on the platform of the microhardness tester and loads of different magnitudes (10, 25 gm) were applied over a fixed interval of time. The indentation time was fixed as 15 s. The transmission spectrum was recorded using a *VARIAN* (Cary 500), UV–Vis–NIR spectrophotometer in the range 200–1100 nm covering the entire near ultraviolet, visible and NIR regions. The nonlinear optical conversion efficiency was tested using a modified setup of Kurtz and Perry [6]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 2.0 mJ and pulse width of 10 ns, the repetition rate being 10 Hz. The crystals of GLN were ground to a uniform particle size of about 125–150 μm and then packed in a capillary of uniform bore and exposed to laser radiations. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation ($\lambda = 532$ nm) from the crystal. The intensity of the green light was measured using a photomultiplier tube. The dielectric study on the single crystals was carried out using the instrument, HIOKI 352-50 LCR HITESTER. A sample of GLN of dimension of $3.54 \times 3.62 \times 1.70$ mm^3 was used for the measurements. Silver coating was applied on the opposite sides of the crystal and was placed between two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was measured for various frequencies, in the range 500 Hz to 5 MHz. The dielectric constant was calculated by using the relation:

$$\varepsilon' = Ct/(\varepsilon_o A)$$

where C is the capacitance, t, the thickness of the sample, ε_o, the permittivity of free space and A, the area of cross-section.

3. Results and discussion

3.1. Single crystal X-ray diffraction

From the single crystal X-ray diffraction data, it was confirmed that the grown crystal belongs to orthorhombic

system with the non-centrosymmetric space group of $P2_12_12_1$. The cell parameters are: $a = 5.601(2)$, $b = 6.090(1)$ and $c = 16.373(4)$ Å. These values agreed well with the reported values [7].

3.2. FTIR studies

The recorded FTIR spectra are depicted in Fig. 3. The observed data were compared with the standard spectra of the functional groups [8]. The broad band in the higher energy region between 3107 and 2603 cm^{-1} is due to NH_3^+ stretching vibrations. The band at 2169 cm^{-1} may be assigned to a combination of the asymmetrical NH_3^+ bending vibration and the torsional oscillation of the NH_3^+ group. The peaks at 1441 and 1041 cm^{-1} are assigned to CH_2 scissoring and wagging, respectively. NO_3^- symmetrical and asymmetrical stretching vibrations are observed at 1041 and 1329 cm^{-1}. The peak at 1391 cm^{-1} can be assigned to the presence of C–H and C–N. The peak at 555 cm^{-1} is assigned to the plane deformation of O–C=O.

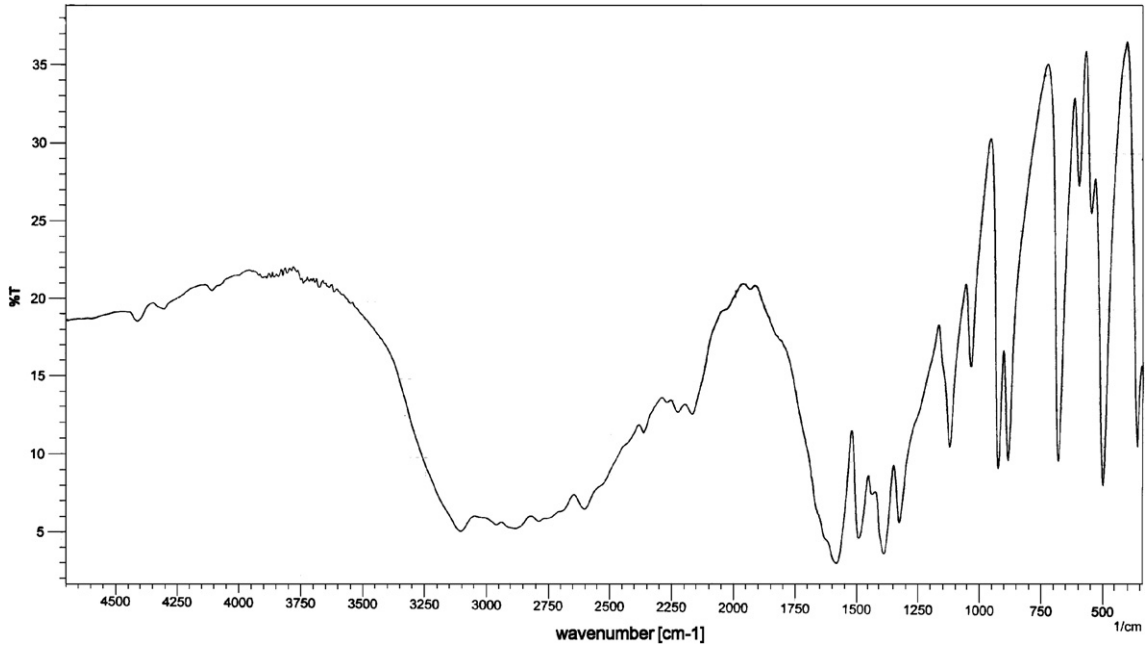

Fig. 3. FTIR of GLN.

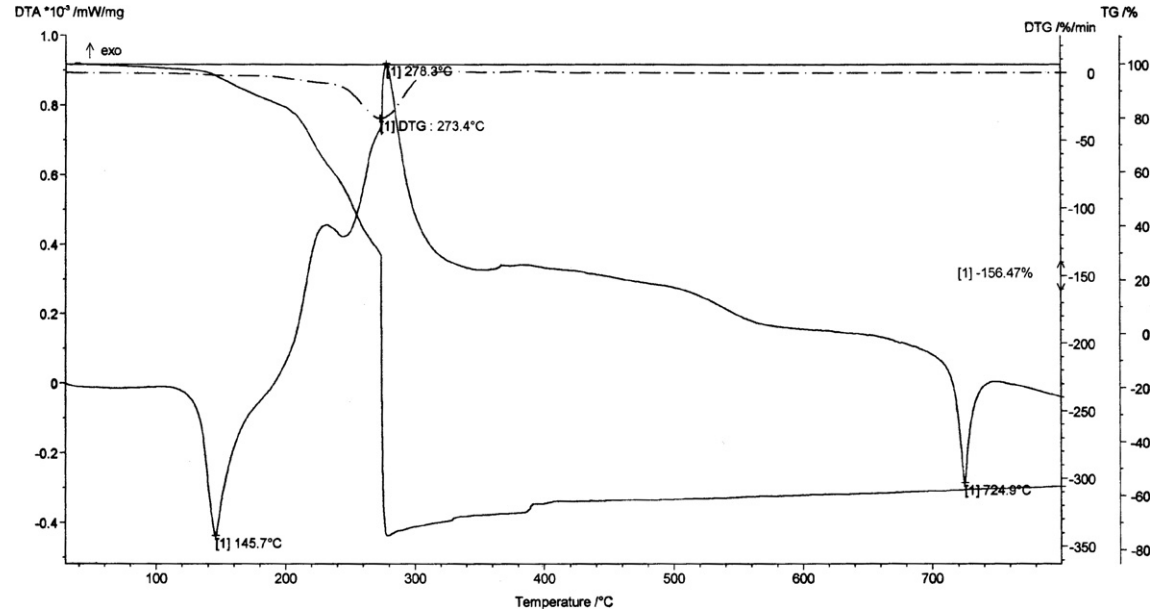

Fig. 4. TGA/DTA of GLN.

3.3. TGA/DTA

In the TGA/DTA spectrum (Fig. 4), an endothermic peak occurred at 145.7 °C, which is due to the melting of the material. Immediately, it starts to decompose. In the initial stages of decomposition, the given thermal energy is utilized to overcome the valence bonding between the glycine anion and nitric acid cation and a loss of mass of 20.2% occurs due to the release of CO, in the temperature range of 146–200 °C. In the second stage, NO_3 got liberated and leads to a gradual weight loss of 44.9% between the temperatures 200 and 260 °C. Afterwards, a sudden weight loss (at 275 °C) occurred due to the decomposition of the remaining molecules simultaneously.

3.4. Microhardness study

The typical Vickers hardness of the crystal was calculated as 65 at 10 g load. When the load was increased to 25 g, cracks developed on the smooth surface of the crystal due to the release of internal stress generated locally by indentation.

3.5. UV–Vis–NIR spectrum

The UV–Vis–NIR transmission spectrum is shown in Fig. 5. The peak at 350 nm is due to the n–π^* transition [9]. The absence of absorption in the region between 230 and 1100 nm shows that these crystals are useful for the second harmonic generation of Nd:YAG laser of wavelength $\lambda = 1064$ nm.

3.6. Powder SHG measurements

The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation ($\lambda = 532$ nm) from the crystal. A second harmonic signal of 50 mV was obtained, while the standard KDP crystal gave a SHG signal of 530 mV/pulse for the same input energy. In the powder sample used, the small crystallites were oriented in different directions. The efficiency of the frequency conversion will vary with the particle size and the orienta-

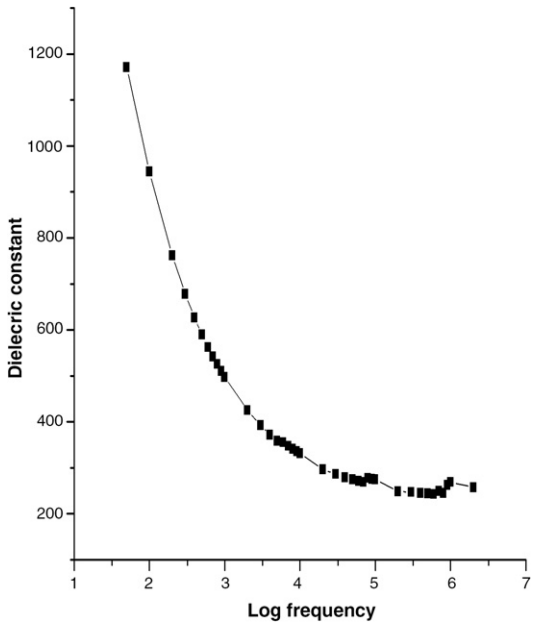

Fig. 6. Variation of dielectric constant of GLN with log frequency.

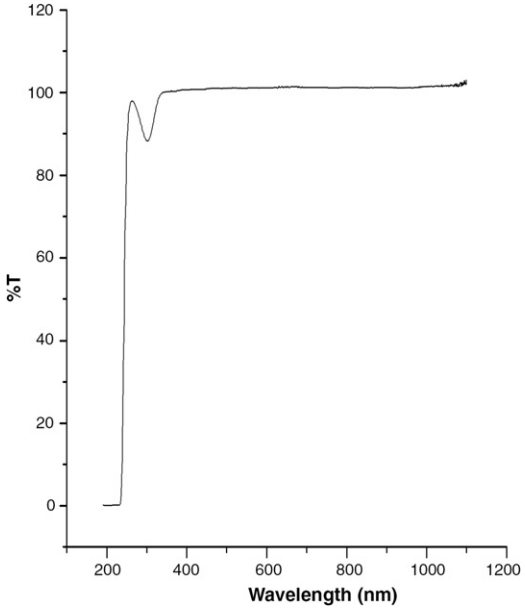

Fig. 5. Transmission spectrum of GLN.

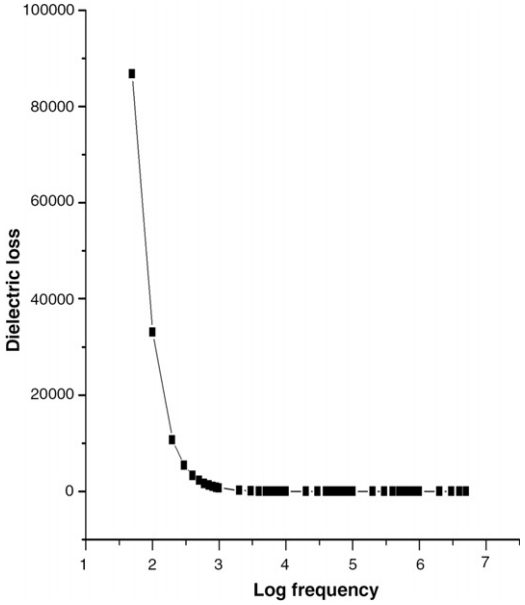

Fig. 7. Variation of dielectric loss of GLN with log frequency.

tion of the crystallites in the capillary tube. Hence, higher efficiencies may be expected to be achieved with single crystals, by optimizing the phase matching [5].

3.7. Dielectric studies

The dielectric constant has higher values in the lower frequency region and then it decreases with the applied frequency (Fig. 6). The value of 'ε' at lower 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. The variation of dielectric loss with frequency is shown in Fig. 7. The low value of dielectric loss with high frequency for these samples suggests that the samples possess enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their applications [10].

4. Conclusions

Transparent crystals of glycine nitrate (GLN), a new NLO material was successfully grown using submerged seed solution method, at room temperature and characterized by single crystal X-ray diffraction. FTIR spectroscopic studies were used to identify the functional groups. Thermal studies showed that the crystals are thermally stable upto 145 °C and optical studies showed that the crystal is transparent to the fundamental and second harmonic of Nd:YAG laser. The SHG efficiency of GLN was investigated using Kurtz and Perry method. Microhardness and dielectric studies were also carried out.

Acknowledgements

The authors thank the DST-FIST Programme and SAMB thanks the Madurai Kamaraj University for providing a Research Fellowship.

References

[1] P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.
[2] A. Datta, S.K. Pati, J. Chem. Phys. 118 (2003) 8420.
[3] K. Jayalakshmi, M.A. Sridhar, J. Shashidhara Prasad, M. Narayan Bhat, S.M. Dharmaprakash, Mol. Cryst. Liq. Cryst. 393 (2003) 95.
[4] K. Ambujam, S. Selvakumar, D. Prem Anand, G. Mohamed, P. Sagayaraj, Cryst. Res. Technol. 41 (2006) 671.
[5] M. Narayan Bhat, S. Dharmaprakash, J. Cryst. Growth 236 (2002) 376.
[6] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.
[7] P. Narayanan, S. Venkataraman, J. Cryst. Mol. Strut. 5 (1975) 15.
[8] G. Socrates, Infrared Characteristic Group Frequencies, Wiley-Interscience, Chichester, 1980.
[9] William Kemp, Organic Spectroscopy, Palgrave Macmillan, 1991.
[10] C. Balarew, R. Duhlew, J. Solid State Chem. 55 (1984) 1.