Materials Science-Poland, *Vol. 27*, *No. 2*, *2009*

Growth and characterization of an NLO material – crystal of triglycine acetate

S.S. HUSSAINI[1], N.R. DHUMANE[1], V.G. DONGRE[2], M.D. SHIRSAT[2*]

[1]Optoelectronics and Sensor Research Laboratory, Department of Physics,
Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431 004 (MS), India

[2]Department of Chemistry, University of Mumbai, Kalina Campus,
Vidyanagari, Santa Cruz (East) Mumbai 400 098 (MS), India

Triglycine acetate (TGAc), a nonlinear optical material, has been synthesized. The second harmonic generation efficiency has been determined by Kurtz's powder test and it was found to be 1.55 times more than potassium dihydrogen phosphate. The solubility studies were carried out in the temperature range 30–55 °C. Single crystals of TGAc have been grown by slow evaporation of solution at 30 °C. The cell parameters were determined by the X-ray diffraction analysis. The UV-visible absorption spectra have been recorded to study the optical transmittance in the range from 200 nm to 800 nm. The Fourier transform infrared analysis identified various functional groups present in the material. The mass spectral analysis was carried out to measure the total molecular weight of the grown crystal. Using thermogravimetric analysis the thermal behaviour was studied.

Key words: *crystal growth; nonlinear optical materials; amino acid*

1. Introduction

In last several years there has been considerable interest in growth and characterization of nonlinear optical materials (NLO) due to their important contribution in areas of optical modulation, optical switching, optical logic, frequency shifting and optical data storage. Several attempts have been made for exploration of nonlinear optical materials which found various applications in optoelectronics [1–7]. The complexes of amino acids and salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of organic amino acids with those of the inorganic acids/salts. Glycine is a simple amino acid which has three polymeric crystalline forms α, β and γ. There are two types of glycine

*Corresponding author, e-mail: mdshirsat_bamu@yahoo.co.in

groups such as glycinium ions and zwitter ion. The zwitterionic structure of glycine is useful for its optical activity [8].

Many NLO crystals grown by mixing amino acids with various organic and inorganic acids have been reported in the literature [9–11]. However, to the best of our knowledge, there is no report on the growth and characterization of TGAc single crystal (mixing glycine with acetic acid). Moreover, our objective was to grow a single crystal of TGAc with enhanced nonlinearity as compared to reported single crystals of this kind. In the present investigation, the synthesized salt – triglycine acetate (TGAc) – was subjected to SHG test and found to possess nonlinearity higher than potassium dihydrogen phosphate (KDP) and many other crystals of amino acids. The bulk single crystal of TGAc was grown by the method of slow evaporation of solution and characterized by various techniques.

2. Experimental

Triglycine acetate was synthesized by adding three moles of glycine of high purity (Kemphasol, 99%) and one mol of annalar grade glacial acetic acid in deionized water. The synthesized salt was purified by repeated crystallization. The solubility test was carried out at constant temperature baths (CTB) (30 ºC, 35 ºC, 40 ºC, 45 ºC, 50 ºC and 55 ºC) stabilized with the accuracy of ±0.01 °C. We observed temperature increase of solubility (Fig. 1). The saturated solution was prepared at 30 °C to grow the single crystal by the slow evaporation technique.

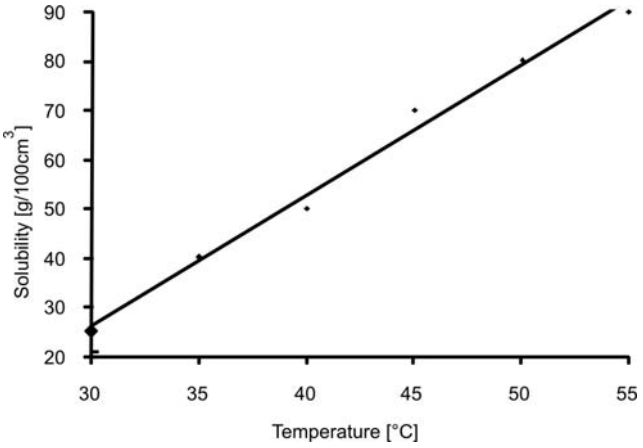

Fig. 1. Solubility curve of TGAc in water

After obtaining the saturation, the prepared solution was filtered with Whatmann filter paper and the solution was placed for slow evaporation at the room temperature. The seed crystals were harvested from the solution after eight days and a suitable seed was selected. The supersaturated solution of TGAc was prepared in 500 cm^3 of deion-

ized water at 30 ºC and kept at this temperature for slow evaporation. After 24 h the selected seed was suspended in the solution. A colourless crystal, harvested after 25 days, was subjected to various characterizations. The photograph of a crystal is shown in Fig. 2.

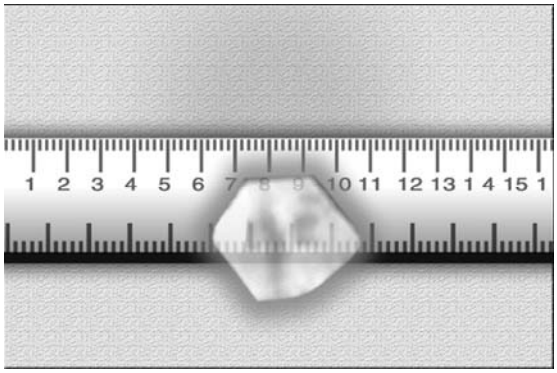

Fig. 2. Photograph of a TGAc crystal

3. Results and discussion

3.1. X-ray diffraction analysis

The single crystal XRD analysis of grown crystals was carried out using the ENRAF NONIUS CAD4 automatic X-ray diffractometer and the collected cell parame-

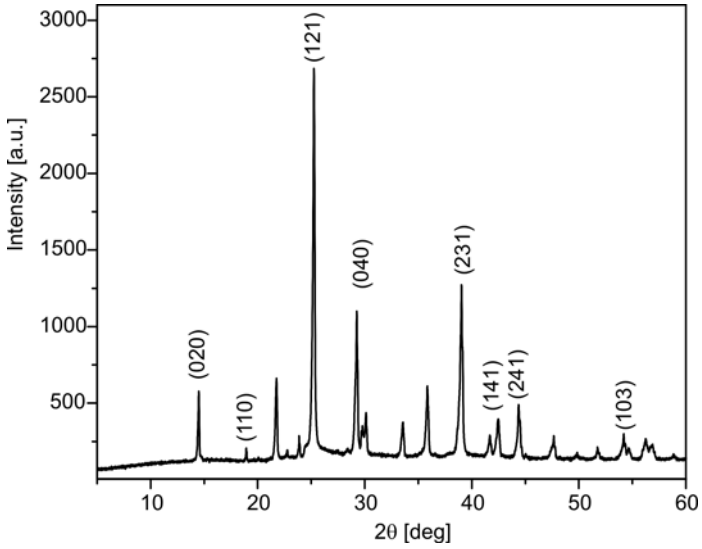

Fig. 3. Powder X-ray spectrum of TGAc

ters are a = 5.1021 Å, b =11.9704 Å, c = 5.4617 Å and $\alpha = \gamma = 90°$, $\beta = 111.7665°$, the cell volume V = 309.7863 Å^3. The powdered sample of the grown crystal was also subjected to powder X-ray diffraction analysis using Panalytical, XPert PRO powder X-ray diffractrometer employing CuK_α radiation (λ = 1.5418 Å).

The peaks observed in the X-ray diffraction spectrum were analysed and the lattice parameters were calculated by the least square fit method. The data obtained by the powder X-ray diffraction analysis is in accordance with the single crystal X-ray diffraction data. It is clear that for the crystal $a \neq b \neq c$, $\alpha = \gamma = 90°$ and $\beta \neq 90°$, which ensures that the grown TGAc crystal is of monoclinic structure. The powder X-ray diffraction pattern is shown in Fig. 3.

3.2. Fourier transform infrared (FTIR) analysis

The IR spectrum of grown TGAc crystal was recorded in the solid state as KBr dispersion using Perkin-Elmer Spectrum-one FT-IR spectrometer (Fig. 4).The spectrum exhibited a characteristic N–H stretching absorption band in the high frequency range between 2787 and 3093 cm^{-1}. The peak at 2787 cm^{-1} is attributed to C–H stretching mode vibration [12].

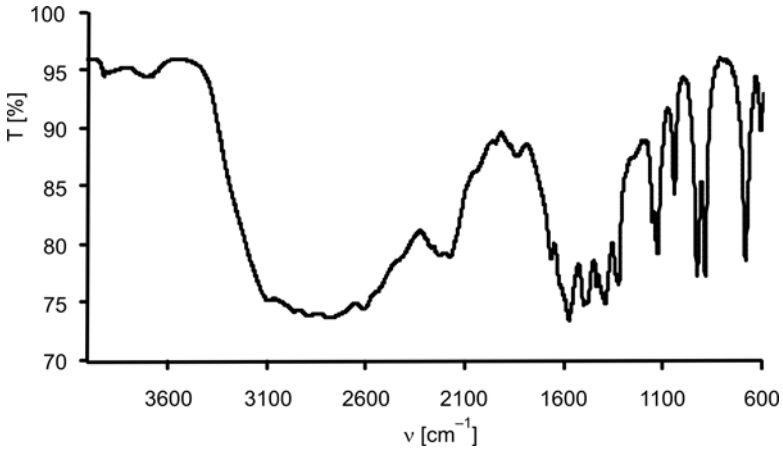

Fig. 4. FT-IR spectrum of TGAc

The absorption band at 1665 cm^{-1} corresponds to C=O stretching mode. The bands between 1574 and 1434 cm^{-1} were due to the asymmetric and symmetric stretching modes of COO^- groups. The bands at 1324 cm^{-1} and 1045 cm^{-1} can be attributed to the presence of COOH groups and stretching vibrations (involving carbon and nitrogen of amino groups), respectively. The torsional vibration of amino group lies between 500 and 556 cm^{-1}. The absorption band between 930 and 1152 cm^{-1} was assigned to asymmetric coupled vibration of acetate and glycine.

3.3. UV-visible spectra

The UV-vis absorption spectrum of TGAc in solution (0.1 mg/cm^3 in methanol) was recorded using a Perkin Elmer Lambda 35 UV spectrophotometer. The UV spectrum

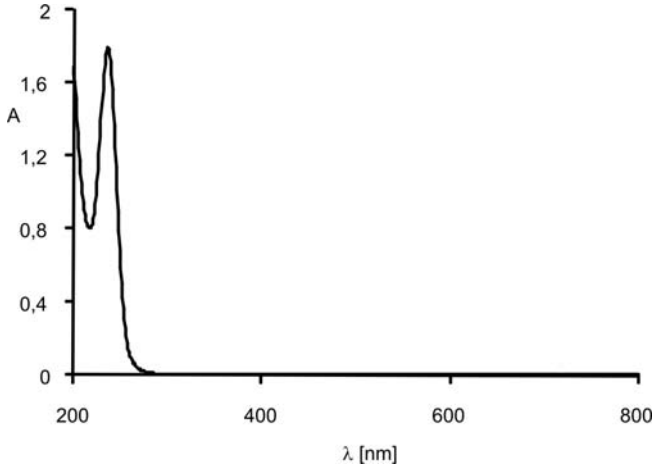

Fig. 5. UV-visible absorption spectra

(Fig. 5) was recorded between 200 to 800 nm; the absorbance was evident below 250 nm. It is assigned to electronic excitation in the COO^- group of glycine. A complete transparency between 230 and 800 nm is interesting, as it is very much required for NLO applications of this crystal [13].

3.4. SHG efficiency test

The Kurtz's Perry technique was employed to test the strength of SHG efficiency of the TGAc crystal by passing the output of an Nd:YAG laser. The laser input pulse

Table 1. Comparison of SHG efficiencies of promising amino acid family crystals

Compound	SHG efficiency
KDP(reference) [10]	1
L-arginine phosphate monohydrate [14]	1.49
L-threonium acetate [10]	1.14
L-alanine [10]	0.2
L-alanine acetate [10]	0.3
L-arginine chloride [10]	0.2
L-arginine bromide [10]	0.3
L-arginine tetrefluroborate [10]	0.54
Triglycine acetale (present paper)	1.55

of 3 mJ with the repetition rate of 10 Hz and the pulse width of 8 ns was used. The photomultiplier tube was used as a detector. The SHG signals of 920 mV and 1430 mV were obtained through KDP and TGAc samples, respectively. Thus, the SHG efficiency of TGAc is 1.55 times higher than that of KDP. A comparison of SHG efficiencies of promising amino acids family crystals is shown in Table 1.

3.5. Thermal studies

The melting point of fine powder of the material was measured as 248±1 °C. The thermogravimetric analysis (TGA) of the triglycine acetate crystal was carried out using TG Q-500 thermogravimetric analyzer at the heating rate of 25 °C/min to 800 °C in a nitrogen inert atmosphere (Fig. 6).

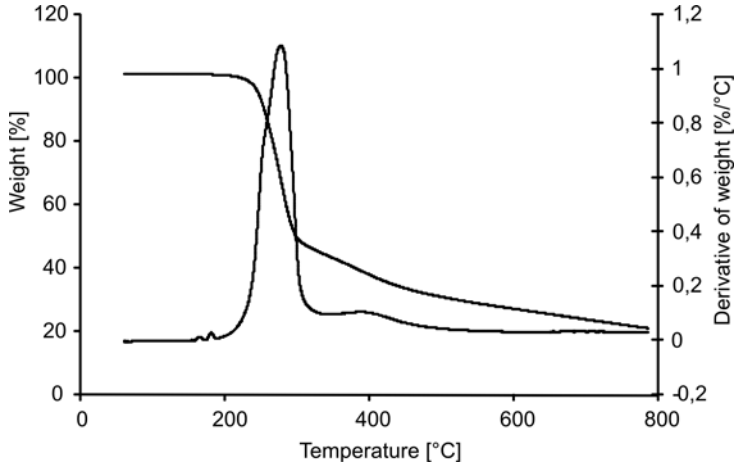

Fig. 6. Thermogram of thermogravimetric analysis

The spectrum shows that there is small weight loss around 180 °C. The material starts decomposing near temperature of 248 °C, which is melting point of the TGAc crystal. The weight loss of 73.25% of 7.432 mg of sample was observed in the temperature range from 248 °C to 306.36 °C. Thereafter residue remains up to of 800 °C. It is clear that the crystal is thermally stable up to 248 °C.

3.6. Mass spectroscopy

The mass spectrum of TGAc was recorded using a thermo-electron LCQ advantage (San Jose, CA, USA) ion trap mass spectrometer. The source voltage was 5 kV and the capillary temperature 375 °C. Nitrogen was used both as a sheath and auxiliary gas. The mass (m) to charge (z) ratio was scanned across the range of m/z from 152 to 400. The mass spectrum is shown in Fig. 7.

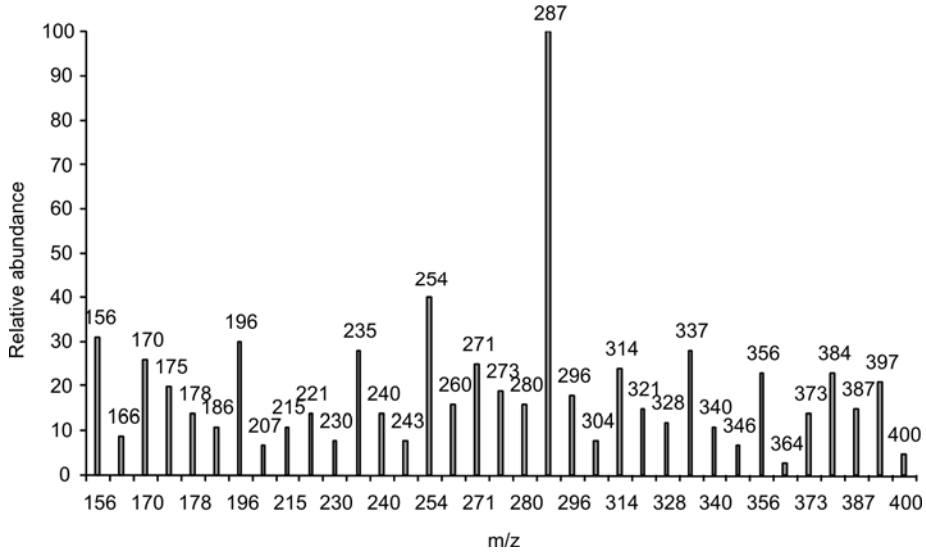

Fig. 7. Mass spectrum of a TGAc crystal

The mass spectrum of TGAc showed a protonated molecular adduct ion peak at m/z = 287 (M + 2H)·$[(NH_2CH_2COOH)_3CH_3COOH + 2H]^+$. The loss of NH_2CH_2 moiety from the molecular ion (285 amu) gives the peak at m/z 255, while the parent ion at m/z 287 undergoes dissociation to form daughter ion at m/z 237 by the loss of $–CO_2$ moiety along with four carboxylic protons. The loss of carboxylic group (–COOH) from the parent ion gives a product ion at m/z = 242. The peak at m/z = 210 can be assigned to the contamination of the impurity: diglycine acetate $(NH_2CH_2COOH)_2 \cdot CH_2COOH$.

4. Conclusions

A single crystal of triglycine acetate (TGAc) was successfully grown using the slow evaporation technique. The X-ray diffraction analysis confirmed the monoclinic structure of the crystal. The minimum absorption in the entire visible region and lower cut off wavelength near 230 nm indicates its applicability NLO material. Various functional groups have been identified by the FTIR spectral analysis. The Kurtz powder test confirmed that SHG efficiency of TGAc is higher than that of KDP and many other crystals of amino acid family. The thermogravimetric analysis confirms the thermal stability of the TGAc up to 248 °C. The mass spectral analysis provides the additional confirmation for formation of this compound.

Acknowledgements

The authors are thankful to the University Grants Commission New Delhi, India, for providing financial assistance. The authors are very grateful to Dr. Babu Varghese, SAIF, Indian Institute of Tech-

nology, Chennai, India, for the single crystal XRD, and Dr. P.K. Das, Indian Institute of Science, Bangalore, India, for the SHG test.

References

[1] DHUMANE N.R., HUSSAINI S.S., NAVARKHALE V.V., SHIRSAT M.D., Cryst. Res. Technol., 41 (2006), 897.
[2] HUSSAINI S.S., DHUMANE N.R., RABBANI G., KARMUSE P., DONGRE V.G., SHIRSAT M.D., Cryst. Res. Technol., 42 (2007), 1110.
[3] HUSSAINI S.S., DHUMANE N.R., DONGRE V.G., SHIRSAT M.D., Optoelectr. Adv. Mater. Rapid Comm., 2 (2008), 108.
[4] HUSSAINI S.S., DHUMANE N.R., DONGRE V.G., GHUGHARE P., SHIRSAT M.D., Optoelectr. Adv. Mater. Rapid Comm., 2 (2007), 707.
[5] SURESH KUMAR B., RAJENDIRAN BABU K., Cryst. Res. Technol., 42 (2007), 607.
[6] MALLIK T., KAR T., BOCELLI G., MUSATTI. A., Cryst..Res. Technol., 41 (2006), 280.
[7] RAMESH BABU R., VIJAYAN N., GOPALAKRISHANAN R., RAMASAMY P., Cryst. Res. Technol., 41 (2006), 405.
[8] AMBUJAM K., RAJARAJAN K., SELVAKUMAR S., VETHA POTHEHER I., JOSEPH G.P., SAGAYARAJ P., J. Cryst. Growth., 286 (2006), 440.
[9] MOHAN KUMAR R., RAJAN BABU D., JAYARAMAN D., JAYAVEL R,, KITAMURA K., J. Cryst Growth., 275 (2005), e1935.
[10] RAMESH KUMAR G., GOKUL RAJ S., MOHAN R., JAYAVAL R., J. Cryst. Growth., 283 (2005), 193.
[11] MURALIDHARAN R., MOHAN KUMAR R., JAYAVAL R., RAMASAMY, P., J..Cryst. Growth., 259 (2003), 321.
[12] SILVERSTEIN R.M., BASSLER G.C, MORRILL T.C., *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1981.
[13] RAJENDRAN K.V., JAYARAMAN D., JAYAVEL R., RAMASAMY P., J. Cryst. Growth., 254 (2003), 461.
[14] MADHAVAN J., ARUNA S, PRABHA K., PACKIUM J.J., JOSEPH G.P., SELVAKUMAR S., SAGAYARAJ P., J. Cryst. Growth., 293 (2006), 409.

Received 6 June 2008
Revised 1 September 2008