Investigation on Growth and Characteristics of Glycine and Glycine Oxalate Crystals

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Abstract— We demonstrate the growth of two different crystals such as glycine and glycine oxalate (GOA) by slow evaporation method. We investigated the physical properties of these crystals using different experimental methods. From the single crystal X-ray diffraction, the formation and type of crystalline structures is determined. Thermal stability of the crystals is determined using the thermo gravimetric and differential thermal analyses (TGA/DTA). TGA/DTA measurements showed that thermal stability of glycine crystals is slightly greater than that of GOA crystals. Z-scan technique suggested that GOA crystals are found to be suitable candidate for optical limiting applications.

Key words: Glycine Oxalate; Z-Scan Technique; Non-Linear Optical Properties; XRD; Slow Evaporation Method

I. INTRODUCTION

Presently researchers are focusing on the fabrication of single crystals having very good non-linear optical (NLO) properties. This is because NLO materials act as vital components in different applications, namely, optical interconnects, high density data storage, optical computing, fiber optic communications etc. [1]. Further, different research groups are looking for the crystals along with excellent mechanical characteristics as well as ability to withstand upon laser irradiation. It is known that crystals belonged to amino acid family are found to exhibit NLO properties. Growth and physical characteristics of different amino acid based crystals such as diglycine hydrobromide, glycine zinc sulphate, glycine sodium nitrate, glycine hydrofluoride, glycine zinc sulphate, glycine oxalate (GOA) have been reported [2-8]. To further explore NLO, structural and thermal properties of the glycine and glycine derivatives, here we report the crystal growth of two different amino acid based crystals such as glycine and GOA. These crystals were subjected to several characterizations using X-ray diffraction (XRD), thermo gravimetric and differential thermal analyses (TGA/DTA) and z-scan technique to investigate their structural, thermal and NLO properties.

II. EXPERIMENTAL

A. Preparation of glycine and GOA crystals

1) Growth of glycine crystals:

Initially appropriate amount of glycine was dissolved in the 100 ml distilled water. The supersaturated solution was obtained by stirring well by the magnetic stirrer. Slow evaporation method was utilized to obtain the crystals from the supersaturated solution having glycine. Glycine crystals were formed once the crystallization reached one month. Fig. 1 represents the photograph of glycine crystals.

2) Growth of GOA crystals:

Glycine (AR Grade) and oxalic acid (AR Grade) were utilized for crystal growth of GOA single crystals. First glycine solution was prepared by solubilizing glycine in the distilled water. Oxalic acid was dissolved in the glycine solution and the blend was carefully stirred using magnetic stirrer. The mixture was allowed to undergo to reaction as given below;

$$C_2H_5NO_2 + H_2C_2O_4 \rightarrow (C_2H_6NO^+_2 \,.\, C_2HO^-_4)$$

Slow evaporation techniques were adapted to crystallize the above solution at room temperature and reaction time was one month. Good quality GOA crystals were obtained and these crystals are shown in Fig. 2.

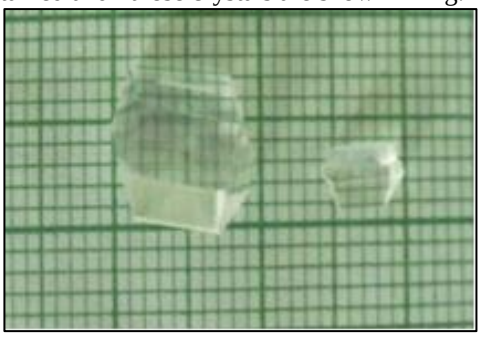

Fig. 1: Photograph of glycine crystals.

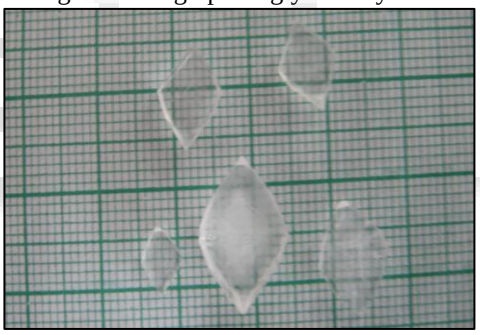

Fig. 2: Photograph of single crystals of GOA.

B. Characterization of crystals:

The grown single crystals (glycine and GOA) have been subjected to single crystal XRD measurements using ENRAF NONIOUS CAD-4 automatic X-ray diffractometer with MoKα radiations (λ = 0.717 Å) to determine crystal structure. TGA and DTA were carried out on glycine and GOA crystals using SII Nanotechnology TGA/DTA 6200 in nitrogen atmosphere at a heating rate of 10°C/minute.

III. RESULTS AND DISCUSSION

A. Characterization of glycine and GOA crystals:

1) Structural studies:

To get insights about structural information of the grown single crystals such as glycine and GOA, single crystal X-ray diffraction experiments were performed on these crystals and results are listed in Table 1. For the case of glycine crystals, the values of cell parameters are determined as follows: a = 5.1 Å, b = 11.9 Å and c = 5.5 Å; α = γ = 90° and β = 104° (Table 1). It is known that in the case of monoclinic system, the lattice parameters are a ≠ b ≠ c and also α = γ = 90° and β

≠ 90°. In the present work, we found that for glycine crystals similar trend of lattice parameters and hence glycine crystals belong to monoclinic system. In addition, volume of unit cell is found to be 308.7 Å3. Similarly, the lattice parameters are calculated for GOA crystals as follows: a = 10.5 Å, b = 5.63 Å and c = 12.0 Å and α = γ = 90°, β = 104°. This implies that GOA crystals also correspond to monoclinic system (Table 1). Unit cell volume of GOA crystals is calculated as 653.4 Å3.

Crystal name	Lattice constant (Å)			Volume (Å^3)	α, β, γ	Crystal structure
	a	*b*	*c*			
Glycine	5.1	11.9	5.5	308.7	$\alpha = \gamma = 90°$, $\beta = 104°$	Monoclinic
GOA	10.5	5.63	12.0	653.4	$\alpha = \gamma = 90°$, $\beta = 104°$	Monoclinic

Table 1: Lattice parameters of glycine and GOA crystals.

2) Thermal properties:

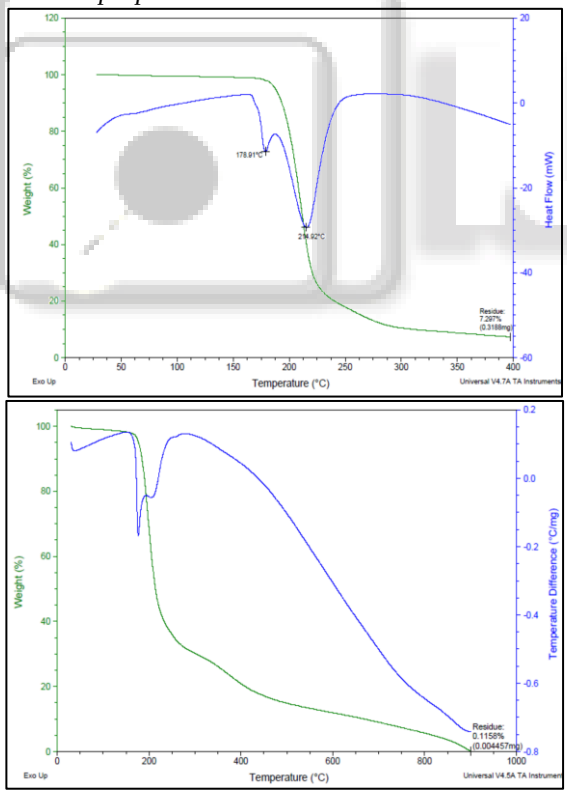

Fig. 4: TG/DTA curves for (a) glycine and (b) GOA crystals.

TGA/DTA measurements were conducted to probe the thermal stability of glycine and GOA crystals. TGA/DTA curves of glycine and GOA crystals were plotted as shown in Fig 4 (a) and (b) respectively. The TGA curve demonstrates that as there is no weight loss for glycine up to 215°C, the glycine has good thermal stability until that temperature. Further the absence of weight loss in the temperature region of about 100°C suggests that the absence of water in the glycine crystal. The DTA curve tells that the melting points of the glycine are 179 and 215°C. On the contrary, it is found from the TGA curve of GOA crystals that the compound GOA has good thermal stability up to 170°C. This observation is consistent with previous observation [8]. Like glycine crystals, the DTA curve for GOA indicate that the two melting points of the GOA crystals; first one at is 170 °C and second is at 210 °C.

3) Z-scan studies:

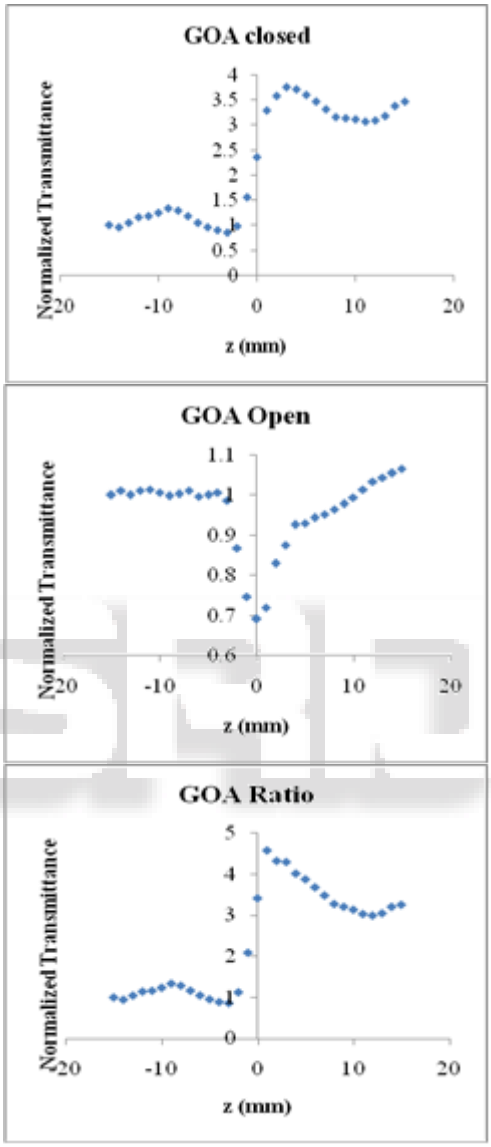

Fig. 5: Z-scan curves of GOA crystals in different configurations. (a) open aperture (b) close aperture and (c) ratio of open and close aperture.

$n_2 \times 10^{-8}$ cm^2/W	$\beta \times 10^{-4}$ cm/W	Re $\chi^{(3)}$ $\times 10^{-5}$ esu	Im $\chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-5}$ esu
5.15	0.748	3.28	4.64	3.33

Table 2: Nonlinear optical properties of GOA crystals.

n2 - Nonlinear refractive index
β - Nonlinear absorption
Re χ3 - Real part of susceptibility
Im χ3 - Imaginary part of susceptibility
χ3 - Nonlinear susceptibilty

To explore the NLO properties (the magnitude of both real and imaginary part of third order nonlinear susceptibility) of the GOA crystals, the Z-scan experiments

were carried out on GOA crystals using a 532 nm diode pumped Nd:YAG laser beam. Z-scan curves in the open and close aperture configurations are shown in Figs. 5 (a) and (b) respectively. Fig. 5 (c) shows the ratio of open and close aperture of GOA. Table 2 lists the NLO properties of GOA. The estimated value of the nonlinear refractive index n_2 is 5.15 × 10^{-8} cm^2/W. The value of nonlinear absorption coefficient (β) determined to be 0.748 × 10^{-4} cm/W and relatively high value of two photon absorptive index exhibits that the GOA crystal has potential for optical limiting applications. The third order susceptibility is 3.33 x 10^{-5} esu.

IV. CONCLUSIONS

By adopting the slow evaporation method, two crystals namely, glycine and GOA were grown at room temperature. From the single crystal XRD studies, it was found that both glycine and GOA crystals have monoclinic crystal structure. TGA/DTA measurements revealed that thermal stability of glycine crystals is slightly greater than that of GOA crystals. Z-scan technique was used to investigate the non-linear optical (NLO) properties of the GOA crystals and suggested that GOA crystal has potential for optical limiting applications.

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REFERENCES

[1] N.J. Long, Angew. Chem., 34, 21-38, 1995.
[2] K. Ambujam, K. Rajarajan, S. Selvakumar, J. Madhavan, G. Mohamed, P. Sagayaraj, Optical Materials, 29, 657–662, 2007.
[3] S. Ravi, P. Subramanian, Solid State Communications, 143, 277–279, 2007.
[4] B. Narayana Moolya, S.M. Dharmapraksh, Materials Letters, 61, 3559–3562, 2007.
[5] K. Selvaraju, R. Valluvan, S. Kumararaman, Materials Letters, 60, 2848–2850, 2006.
[6] Ra. Shanmugavadivua, G. Ravia,, A. Nixon Azariah, Journal of Physics and Chemistry of Solids, 67, 1858–1861, 2006.
[7] S. Palaniswamy and O.N. Balasundaram, Asian Journal of Chemistry, 21, 3459-3462, 2009.
[8] K. J. Arun, S. Jayalekshmi, Optoelectronics and Advanced Materials – Rapid Communications 2, 701 – 706, 2008.

