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Thermal parameter studies on solution grown food derivative amino acid based formate and oxalate crystals

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Abstract: Amino acids are having important role in the foods and nutrients. Glycine has the major role and physical study of these glycine materials is essential. In the present study, triglycine formate and triglycine oxalate crystals were grown by slow evaporation method. The grown crystals were characterized by CHNS analysis and powder X-ray diffraction. CHNS results showed that all the elements are presented in the grown crystals with appropriate value. Powder X-ray diffraction pattern revealed that the grown crystals belong to monoclinic structure. Thermal parameters like Debye–Waller factor, mean-square amplitude of vibration and Debye temperature were determined using powder X-ray diffraction data. The thermal parameters of triglycine formate have lower than the triglycine oxalate single crystals.

Keywords: formate crystals, oxalate crystal, PXRD, lattice parameters, Debye–Waller factors, Debye temperatures.

1. Introduction

Amino acids attract a great deal of attention in field of food and nutrients and are required for the synthesis of body protein and other important nitrogen-containing compounds, such as creatine, peptide hormones, and some neurotransmitters. The biological process of the amino acids is that the excess amount of consuming amino acids need for the synthesis of nitrogenous tissue constituents and these are degraded as urea. The keto acids left after the removal of the amino groups are either utilized directly as sources of energy or converted to carbohydrates or fat. Hence, degradation is a process that renders an object useless or less useful over time. Degradation can be caused by many different means, and it is almost always considered an undesirable process. Chemical degradation is another process that can cause a material to become less useful over time [1]. In addition, the study of physical properties of the amino acid is interesting due to its applications in the field of Engineering and Applications as optical switches, optical modulators, optical communications, optical data storage etc. [2-4]. Among the various amino acids such as histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine, Glycine (NH_2CH_2COOH) is the simplest amino acid, exhibits three polymeric crystalline forms α, β and γ [5-6]. Few reports were related to the physical properties of amino acid based crystals such as acetylated alanine, acetylated glutamic acid, amino acid doped Cu_2O Crystals [7-9]. In the present study, we grew the triglycine formate (TGF) and triglycine oxalate (TGO) crystals.

The Debye temperature can be estimated from the experimental data like specific heat, elastic constants, X-ray and neutron diffraction intensities, etc. Also, it is possible to estimate from the data like melting points, compressibility and micro hardness using semi empirical

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relations [10]. However, the values obtained from melting points, compressibility and micro hardness are not as accurate as those obtained from specific heat or elastic constants. Blackman and Alers [11] have reviewed the various methods of determination of Debye temperatures and proposed an efficient method of determining the Debye temperature is from the Debye-Waller factor using the X-ray powder diffraction data [12 - 13]. By this method, the Debye temperature has been estimated for tartaric acid crystals [14], tartrate crystals [15] and alkali halides [16 -18] etc. As this method is suitable for any crystal system, it can be used to determine the Debye temperature for the solution grown triglycine formate and triglycine oxalate crystals. The CHNS analysis of the grown crystals was determined to identify the expected atoms in the grown crystals. X-ray diffraction data were collected from powder samples of the grown crystals and used for the estimation of lattice variation and thermal parameters like mean Debye-Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency.

2. Materials and Method

Analytical reagent grade glycine ($C_2H_5NO_2$), formic acid (CH_2O_2) and oxalic acid ($C_2H_2O_4$) were used for the growth of single crystals. The required amount substances were taken in the ratio 3:1 for the growth of triglycine formate and triglycine oxalate crystals. The general equation for the formation of triglycine formate and triglycine oxalate crystals is shown in equation (1) and (2) respectively.

$$3\,C_2H_5NO_2 + CH_2O_2 \longrightarrow C_7H_{17}N_3O_8 \quad (1)$$

$$3\,C_2H_5NO_2 + C_2H_2O_4 \longrightarrow C_8H_{17}N_3O_{10} \quad (2)$$

The saturated solution of triglycine formate and triglycine oxalate was prepared by mixing the required amount of glycine, formic acid and oxalic acid in the deionised water separately. Both the solutions were stirred individually with a magnetic stirrer for one hour to get the homogeneous mixer at room temperature. The solution was filtered and transferred to the growth vessel. The prepared solution was kept in a constant temperature bath at optimized temperature. A transparent crystal of triglycine formate and triglycine oxalate with good morphological perfection was collected and used for the characterization studies. The figure 1 and 2 represents the solution grown triglycine formate and triglycine oxalate single crystal respectively.

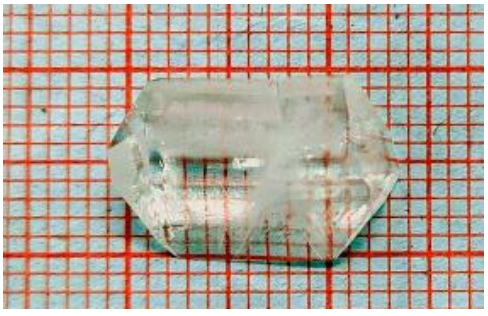

Fig. 1 Photograph of triglycine formate single crystals

Fig. 2 Photograph of triglycine oxalate single crystals

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The grown crystals were subjected to CHNS analyzer (ELEMENTAR Vario EL III) and EDAX(Hitachi S4700) in order to find the elemental composition of the sample. X-ray diffraction data were collected from powder samples of crystals using an automated diffractometer with monochromated CuK_α (λ = 1.5418 Å) radiation and scintillation counter at a temperature of 25±1 ◦C. The reflections were indexed using powder x [19] software. Lattice parameters were determined from the indexed data using high angle reflections.

3. Result and discussion

The elements presented in the grown crystals of TGF and TGO were determined using the result obtained from CHNS analysis.

The expected amount of percentage such as carbon (C), hydrogen (H) and nitrogen (N) were analysed and the analytical data of the grown crystals are tabulated in Table 1. The chemical formula for the grown triglycine formate and triglycine oxalate crystal is $C_7H_{17}N_3O_8$ and $C_8H_{17}N_3O_{10}$ respectively. It is understood from the table 1, the calculated percentage of carbon, hydrogen and nitrogen are almost equal to the experimental values and not exceeding the recommended percentage [20]. Hence it is confirmed that the grown crystals are triglycine formate and triglycine oxalate.

Table 1 Comparison of experimental and calculated atomic weight percentage of TGF and TGO crystals

Triglycine formate crystal			**Triglycine oxalate crystal**		
Elements	Calculated value (%)	Experimental value (%)	Elements	Calculated value (%)	Experimental value (%)
Carbon	30.47	29.78	**Carbon**	31.53	31.00
Hydrogen	5.43	6.11	**Hydrogen**	6.56	6.32
nitrogen	13.33	13.04	**Nitrogen**	15.26	15.49

The indexed XRD patterns of triglycine formate and triglycine oxalate crystals are presented in figure 2 and 3 respectively.

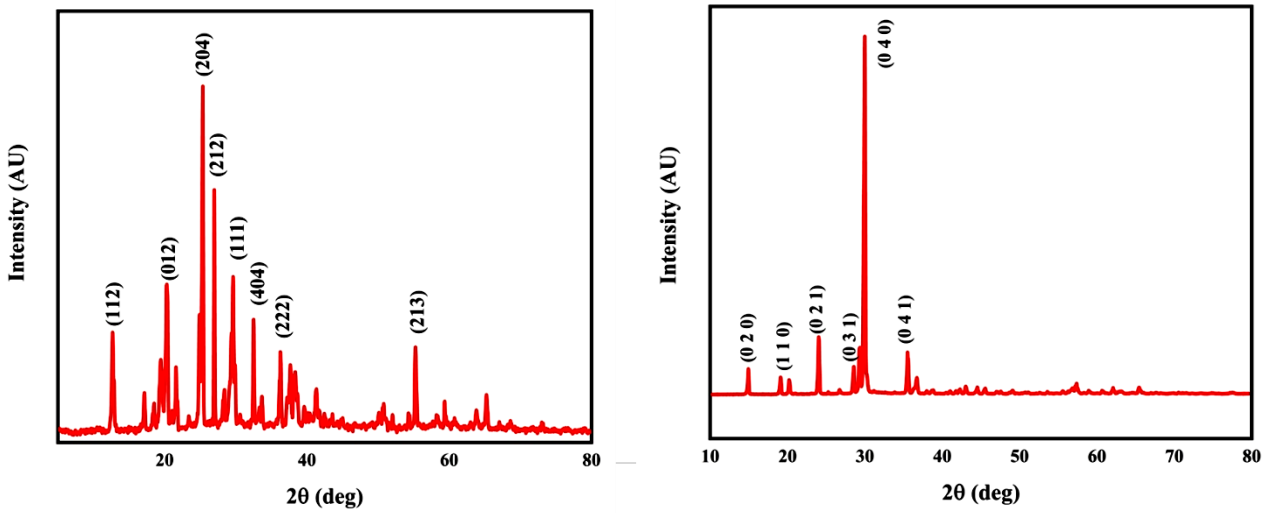

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Fig. 3 Indexed PXRD pattern of TGF crystals

Fig. 4 Indexed PXRD pattern of TGO crystals

The X ray diffraction patterns of TGF and TGO crystals were compared with the JCPDS file of glycine [21], glycine formate [22] and glycinium oxalate [23] and it is concluded that the triglycine formate and triglycine oxalate crystals are belong to monoclinic structure. Lattice constant and lattice volume of the solution grown TGF and TGO crystals were determined and tabulated in table 2.

Table 2: Lattice parameter of TGF and TGO crystals

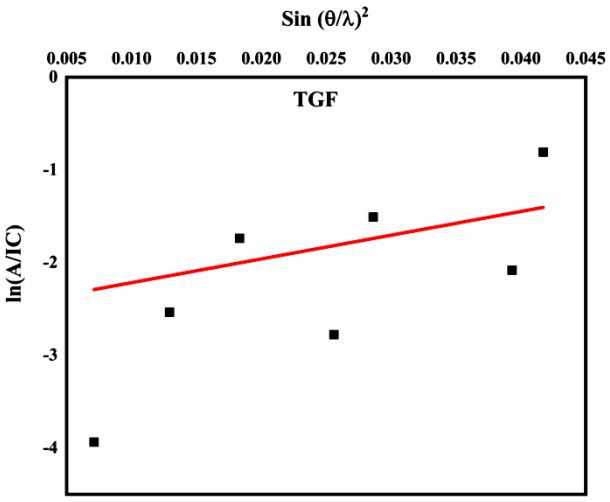
System	a (Å)	b (Å)	c (Å)	V $(Å)^3$
Triglycine formate	5.488	11.988	5.217	318.05
Triglycine oxalate	10.709	5.852	12.364	719.67

The mean Debye–Waller factors (B_{obs}) were determined by the Wilson plot method. For the calculation of structure factors, the atomic scattering factors were taken from the literature [23 – 24]. For triglycine formate and triglycine oxalate crystals, the structure factors are:

$$F = 14f_C + 32f_H + 16f_O + 6f_N \quad (3)$$

$$F = 16f_C + 34f_H + 20f_O + 6f_N \quad (4)$$

The mean Debye-Waller factor for the systems considered in the present study was found by using the Wilson plot method [25]. The Wilson plot of TGF and TGO crystals were given in figure 5 and 6.



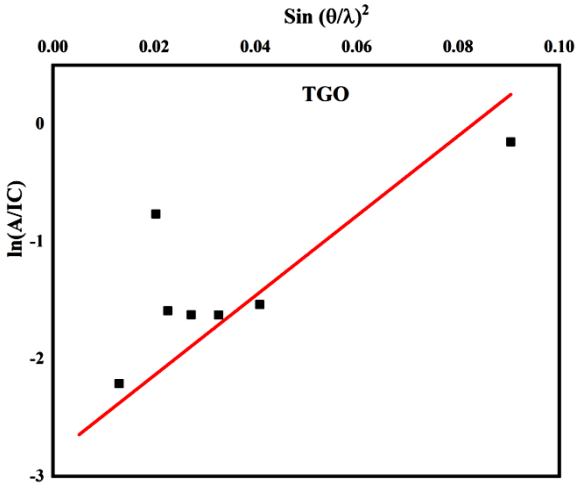


Fig. 5 Wilson plot of TGF crystals

Fig. 6 Wilson plot of TGO crystals

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Mean square amplitudes of vibration and mean Debye temperatures were then calculated using the following relations: We have,

$$B = 8\pi^2(u^2) \quad (5)$$

where $<u^2>$ is the mean square amplitude of vibration. From the Debye-Waller theory,

$$B = 6h^2\mathrm{W}(x)/(mkT) \quad (6)$$

where h is the Planck's constant, m is the mean atomic mass of the crystal, k is the Boltzmann'sconstant and T is the absolute temperature. We have,

$$\mathrm{W}(x) = \{\varphi(x)/x^2\} + (x/4) \quad (7)$$

where $x = \theta_D/T$ (θ_D is the Debye temperature) and

$$\varphi\,(x) = \int^{x}\{e^y/(1 - e^y)\}\,dy \quad (8)$$

The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill [26]. From $W(x)$, x was found from the tables mentioned above. From x, Debye temperatures (θ_D) for systems considered in the present study were calculated. Knowing the Debye temperatures, the Debye frequencies were calculated using the relation [27],

$$\theta_D = f_D(h/k) \quad (9)$$

where h is Planck's constant and k is Boltzmann's constant.

The Debye-Waller factor (B), mean square amplitude of vibration ((u^2)), Debye temperature (θ_D) and Debye frequency (f_D) values of TGF and TGO crystals are provided in Table 3.

Table 3: Thermal parameter of TGF and TGO crystals

System	B (Å^2)	(u^2) (Å^2)	θ_D (K)	$f_D(10^{12}$Hz)
Triglycine formate	12.80	0.1623	118.0	2.457
Triglycine oxalate	16.98	0.2156	206.5	4.007

4. Conclusion

Triglycine formate and triglycine oxalate crystals were grown by slow evaporation method from aqueous solution. CHNS results showed the presence of the all the elements with the respective percentage and confirmed the grown crystals are triglycine formate and triglycine oxalate. X- ray diffraction studies of all the grown crystals were carried out and the lattice parameter were determined. The indexed XRD pattern of grown TGF and TGO crystal suggested that these crystals belong to monoclinic structure. Using the XRD data, mean Debye-

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Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency were determined for solution grown triglycine formate and triglycine oxalate crystals. The thermal parameters such as mean Debye-Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency of triglycine formate have lower value than the thermal parameters of triglycine oxalate crystals.

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