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Growth and Characterization of β-Alanine Oxalate—A New Organic Single Crystal

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ABSTRACT

A new organic single crystal of β-Alanine Oxalate (BAO) has been grown from solution by slow evaporation technique. Transparent, colourless crystals of size upto 11 × 9 × 4 mm^3 were obtained. Formation of the new crystal has been confirmed by single crystal XRD and FTIR spectra. The grown crystals have been subjected to powder X-ray diffraction studies to identify the crystalline nature. Single crystal X-ray diffractometer was utilized to measure unit cell parameters and to confirm the crystal structure. BAO belongs to monoclinic system with lattice parameters a = 22.335 Å, b = 5.697 Å, c = 13.993 Å, $\alpha = 90˚$, $\beta = 115.37˚$, $\gamma = 90˚$, and volume of the unit cell, V = 1609 $Å^3$. The functional groups are confirmed by FTIR vibrational analysis. Optical transmission spectra revealed the optical properties of the grown crystal. Transmission spectrum reveals that the crystal has low UV cut-off of 205 nm and has a good transmittance in the entire visible region enabling its use in optical applications. There is no absorption in the entire visible region. Mechanical strength of the grown material is tested by hardness studies. The value of hardness increases when the applied load is increased.

Keywords: Amino Acid; X-Ray Diffraction; Lattice Parameters; FTIR; Transmittance; Microhardness; Organic Crystal; SHG

1. Introduction

Amino acids and their complexes are the organic or semi-organic materials that have attracted great attention due to their ability in ease of processing in the assembly of optical devices. The complete understanding of the optical properties of amino acid crystals, as well as other organic crystals, still requires more attention [1-7]. 3-Aminopropionic acid is commonly known as β-alanine with molecular formula C3H7NO2 and in which the amino group is at the β-position from the carboxylate group [8-10]. Supplementation with β-alanine has been shown to increase the concentration of carosine in muscles, decrease in fatigue in athletes and increase total muscular work done. β-alanine is purely a synthetic amino acid and it is a positional isomer of L-alanine [11,12]. It forms crystalline complexes with organic, inorganic acids or salts. In this paper, we report for the first time the growth and characterization of a new organic crystal viz. β-alanine oxalate and the results are presented.

2. Experimental Procedure

2.1. Growth

β-alanine and oxalic acid were taken in the molar ratio of 1:1 and the calculated amounts of β-alanine and oxalic acid were dissolved thoroughly in de-ionized water at room temperature. A saturated solution was prepared and the solution was filtered using a Whatmann filter paper.

For the growth, the filtered solution in a beaker was allowed for slow evaporation. Good colourless, transparent single crystals were obtained within a period of 15 - 20 days. The grown crystal is displayed in **Figure 1**. The size of a grown crystal is observed to be 11 × 9 × 4 mm^3. Re-crystallization was carried out twice to improve the purity of the sample.

2.2. Instrumentation

Powder X-ray diffraction measurement was taken using an automated X-ray powder diffractometer(PANalytical) with nickel filtered, monchromated CuK_α radiation (λ = 1.5406 Å). The XRD pattern was taken after the grown crystal was crushed into fine powder. The Fourier Transform Infrared (FTIR) spectrum was recorded using

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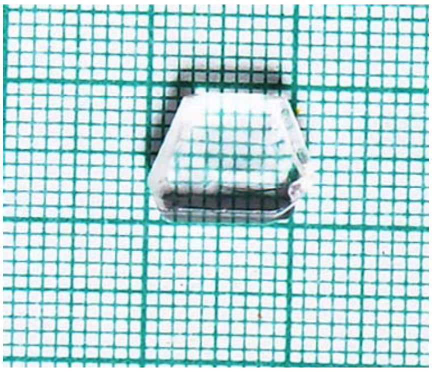

Figure 1. Photograph of BAO crystal.

SHIMADZU 8400 S. The sample was prepared by pressing BAO with KBr into a pellet form. The UV-Vis spectrum of BAO crystal was recorded in the wavelength range 190 nm - 1100 nm using Perkin Elmer Lambda 35 spectrometer.

3. Results and Discussion

3.1. Solubility

The solubility of BAO was measured in the temperature range from room temperature to 55˚C. A volume of 50 ml of water was taken in a container and re-crystallized salt was added. The temperature of the solution was maintained above the chosen constant temperature and continuously stirred using a magnetic stirrer to ensure homogeneous temperature and concentration throughout the entire region of the solution. Once the saturation was reached, the equilibrium concentration of the solute was analyzed gravimetrically [13]. The experiment was carried out for various temperatures from room temperature to 55˚C in steps of 5˚C and the solubility curve was drawn and it is presented in the **Figure 2**. The solubility curve indicates that BAO crystal has positive temperature coefficient of solubility.

3.2. XRD Analysis

From the single crystal X-ray diffraction analysis, it is found that the BAO crystallizes in monoclinic system with lattice parameters a = 22.335 Å, b = 5.697 Å, c = 13.993 Å, α = 90˚, β = 115.37˚, γ = 90˚, and volume of the unit cell, V = 1609 Å^3. In order to study the crystal structure of BAO the grown sample was subjected to powder X-ray diffraction studies with a high resolution PANalytical X'pert PRO diffractometer. Powder XRD pattern of BAO sample is shown in **Figure 3**. All the reflections of powder XRD pattern of this work were indexed using the TREOR and INDEXING software packages following the procedure of Lipson and Steeple [14]. The values of 2θ, hkl values and d-values etc are presented in the **Table 1**.

3.3. FTIR Analysis

FTIR study is used to identify the functional groups of the samples. In the FTIR spectrum (**Figure 4**), the band at 2927 cm^{-1} is on the high frequency side of the broad absorption. The deformation vibration of the water molecules was found at 1525 cm^{-1}. The broad bands due to the in-plane bending vibrations (δ OH) of the O-H···O bending bonds are located at 1128 cm^{-1}. The out-of-plane bending modes of the O-H···O hydrogen bonds (γ OH) were found at 918 and 781 cm^{-1}. The ν_a COO mode gives rise to the absorption observed at 1627 cm^{-1}. The strong band 1402 cm^{-1} is attributed to the ν_s COO$^-$ mode. The carboxylic groups scissoring modes (δ COO$^-$) are expected in the region of 500 - 750 cm^{-1}. Weak bonds are visible at 648 cm^{-1}. The complete absorption bands and their assignments for the grown BAO sample are provided in the **Table 2**.

3.4. UV Visible Spectral Studies

The UV-Vis analysis was made between 190 and 1100 nm, which covers near ultraviolet (200 nm - 400 nm), Visible (400 nm - 800 nm) and then Far-Infrared (800 - 1200 nm) regions. The plot of % of transmittance versus

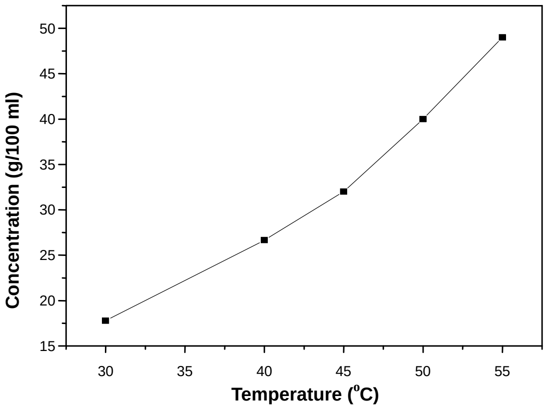

Figure 2. Solubility curve of BAO crystal.

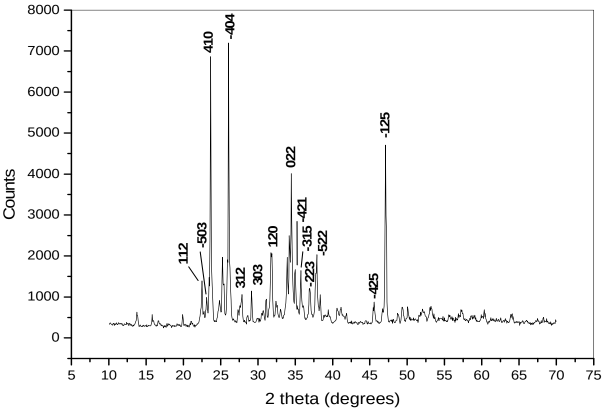

Figure 3. Powder XRD pattern of BAO crystal.

Table 1. The values of 2*θ*, hkl and d-values for BAO crystal.

2*θ* (degrees)	d (cal) Å	d (obs) Å	hkl
13.81695	6.32176	6.40386	002
15.86843	5.58079	5.58028	–401
16.67197	5.525853	5.31310	–111
17.98822	4.96093	4.92718	210
19.90698	4.43471	4.45638	–501
21.07639	4.2145	4.21169	003
22.47157	3.92216	3.95326	112
23.09904	3.85449	3.84724	–503
23.67687	3.77703	3.75467	410
24.81665	3.60886	3.58474	–213
25.2999	3.49944	3.51735	–511
26.07443	3.41713	3.41461	–404
27.36215	3.25637	3.25676	–504
27.84415	3.19245	3.20147	312
28.62254	3.16088	3.11615	004
29.15924	3.03416	3.06000	303
29.92589	2.97881	2.98333	–314
30.71410	2.92249	3.90855	213
31.11264	2.86315	2.87219	412
31.80475	2.82054	2.81125	120
32.47677	2.74613	2.75468	–221
33.05522	2.70392	2.70770	204
34.5039	2.59704	2.59752	022
35.01030	2.53712	2.56084	–421
35.75416	2.50847	2.50925	–315
36.94224	2.43091	2.43124	–223
37.83470	2.38321	2.37591	–522
38.93460	2.31125	2.31129	015
39.42319	2.28173	2.28376	123
40.63857	2.20793	2.21822	–324
41.11312	2.19436	2.19371	521
41.87151	2.15957	2.15571	422
45.54444	1.99303	1.99003	–425
47.12085	1.94149	1.92707	–125
48.70484	1.86774	1.86803	–231
49.35870	1.84537	1.84481	415
50.10238	1.81872	1.81915	032
52.06304	1.75284	1.75516	–333
53.19255	1.71831	1.72052	530
54.36710	1.68578	1.68610	524
55.62736	1.65202	1.65084	–134
57.32108	1.60938	1.60602	425
58.65760	1.57055	1.57258	–335
60.39421	1.53397	1.53144	525
63.95376	1.45802	1.45452	434
67.40114	1.38826	1.38826	–342
68.25821	1.37290	1.37290	–442

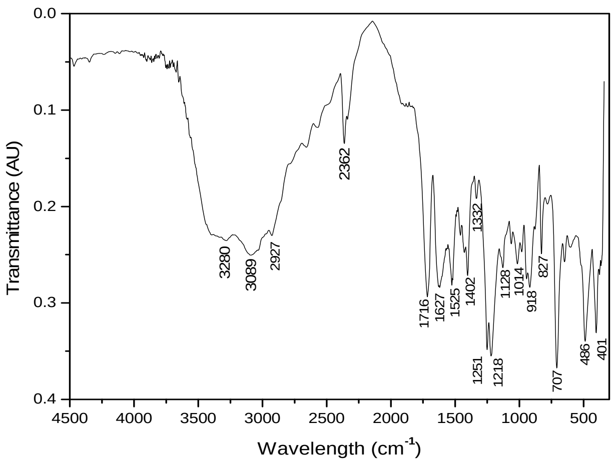

Figure 4. FTIR spectrum for the grown crystal of BAO.

Table 2. FTIR assignments for BAO crystal.

Wave number in cm^{-1}	Band assignments
3280	va H_2O
3089	vs H_2O
2927	ν N-H···O
1716	va C = O (*β*-alanine)
1627	va C = O (acid)
1525	*δ* H_2O
1458	*δ* C H_2/*δ* N-H···O
1429	*δ* C H_2
1402	vs COO-(acid)
1332	*ω* C H_2
1251	ν CO-H
1218	ν CO-H
1128	*δ* OH, ν C H_2-C H_2
1062	ν C-H
1014	*ρ* C H_2
981	*P* NH_3^+
918	*P* NH_3^+ , *γ* OH
827	ν C-C
781	*γ* OH
707	*δ* COO
648	*δ* COO^-
486	*ω* COO^-
401	*δ* COO^-

wavelength is shown in **Figure 5**. The absorbance is not registered until the wavelength 205 nm is reached from 1100 nm. At 205 nm, a sharp fall of transmittance was observed indicating a single transition in the near UV region. The nearly sharp fall in transmittance at 205 nm suggests nearly similar distribution of energies among all molecules of *β*-alanine oxalate single crystal, which otherwise will yield a gradual decrease in the transmittance from the longer wavelength to 205 nm. The plot of % of absorbance vs wavelength is shown in **Figure 6**. From the graph, it is observed that there is no absorption in the entire UV and visible region.

3.5. Thermal Studies

Differental Thermal (DTA)/Thermaogravimetric (TG)

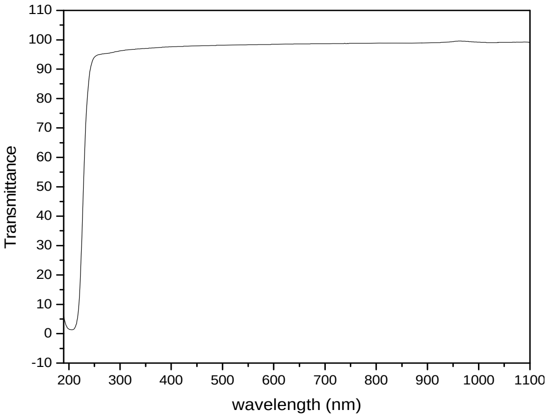

Figure 5. UV-vis-NIR transmittance spectrum for the grown BAO crystal.

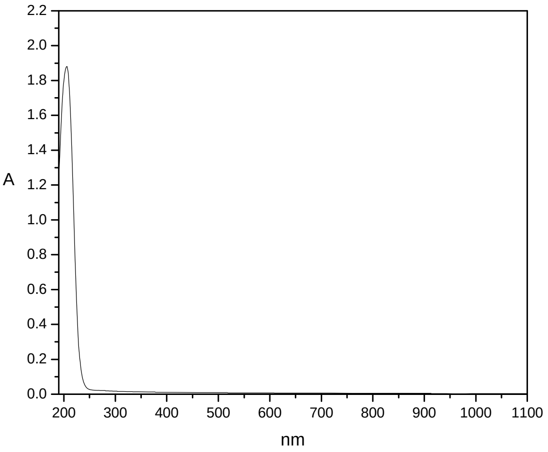

Figure 6. Absorbance spectrum of BAO crystal

analyses were carried out on the BAO samples to look for possible phase transitions and to determine the melting point. The thermal analysis was carried out in the temperature between 30° and 1000˚C. The TG/DTA response curve of BAO is shown in **Figure 7**. The DTA curve shows a major endothermic peak observed at around 172˚C and it may attributed to the melting of the material. The sharp DTA peak at 545˚C is attributed to the volatilization of the material the other endothermic or exothermic peaks observed, coincide exactly with the decomposition observed in the TGA curve. In the TGA trace, there is a major weight loss of 77% starting at about 182˚C and ending at 353˚C. It is due to the decomposition and volatilization of the compound. The next weight loss of about 13% occurs between 353˚C and 595˚C shows that the decomposition is almost complete. There is one more weight loss between 595˚C and 980˚C is due to the decomposition of the residue that is left over after the major weight loss which corresponds to 5%.

In order to confirm the melting and volatilization of the compound without decomposition, DSC analysis was carried out between 20˚C and 1000˚C. The DSC trace is shown in **Figure 8**. The exotherm at 172˚C is assigned to melting of the material and a sharp endothermic peak at 548˚C is assigned to volatilization based on the results obtained with DTA curve.

3.6. Hardness Measurements

Hardness is the resistance offered by a material to plastic deformation caused by scratching or by indenta tion. In ideal circumstances, measured hardness value should be

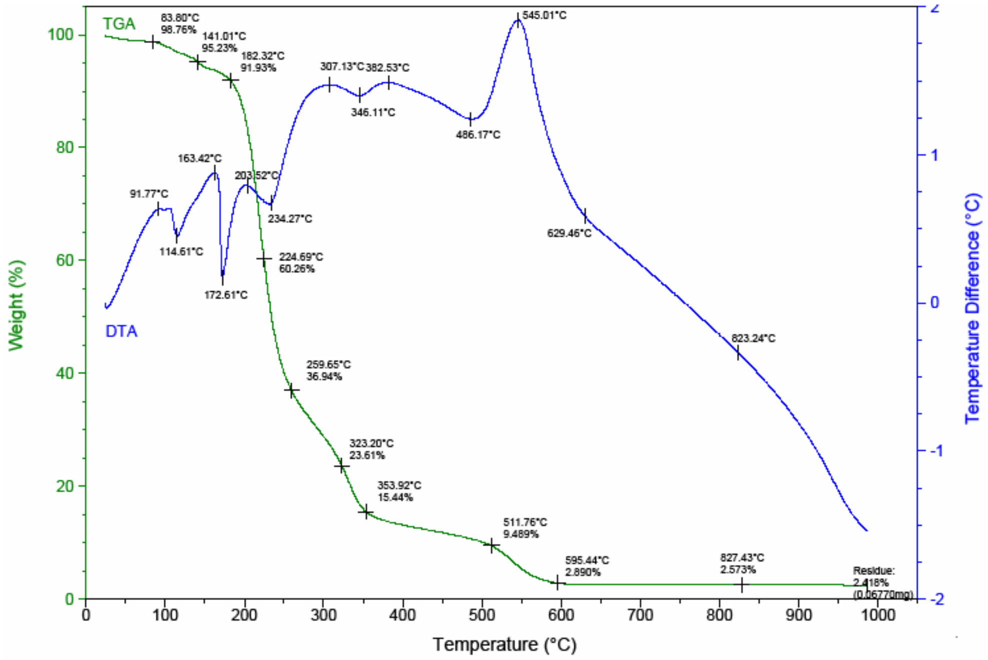

Figure 7. TGA and DTA curves of BAO sample.

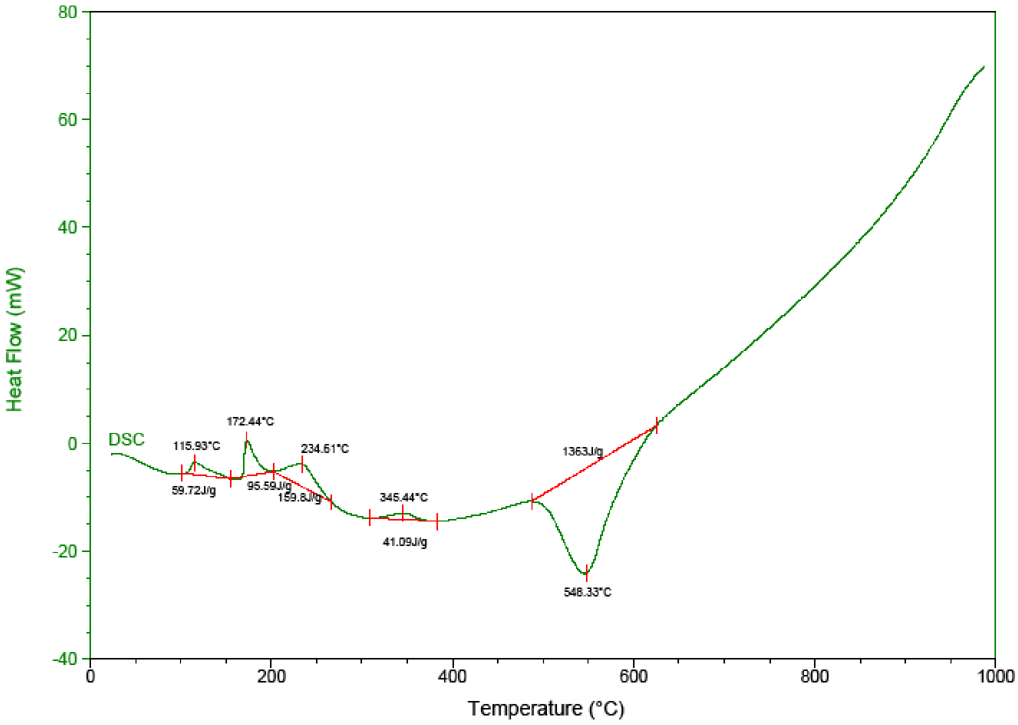

Figure 8. DSC curve of BAO sample.

independent of applied load. But in practice, load dependence is observed. In this work, the selected smooth surface of a BAO crystal was used for microhardness measurements at room temperature, using a Vickers micro hardness tester (mhp-100) attached to an incident-light microscope (Leitz-Wetzler microscope) keeping the indentor at right angles to the crystal plane for 10 s in all cases. An average of 10 diagonal length of the indentation mark was measured using an optical micrometer eyepiece at a magnification of 500:1. The Vickers microhardness number was calculated using the relation H_v = 1.8544 P/d kg/mm^2 where P is the applied load and d is the diagonal length of the indentation impression [15,16]. A plot of H_v versus load is shown in **Figure 9**. As the load is increased, there is an increase in the hardness. The increase of microhardness with increasing load is in agreement with the Indentation Size Effect (ISE) as reported in the literature [17].

3.7. Second Harmonic Generation (SHG) Test

The SHG test for the grown BAO crystal was carried out by using powder Kurtz and Perry technique [18]. The crystal was ground into a homogenous powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser beam of wavelength 1064 nm (pulse width 6 ns) was allowed to strike the sample cell normally. A sample of potassium dihydrogen phosphate (KDP) also powdered and was used for the same experiment as a reference material in the SHG measurement.

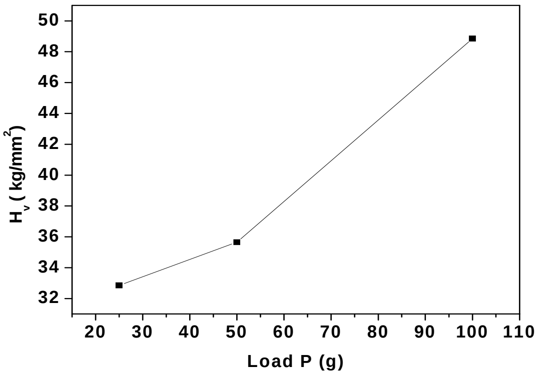

Figure 9. Plot of Hv versus load for BAO crystal.

From the experiment, it is noticed that there is no green light (no SHG emission) emitted from the sample and this gives the conclusion that the grown BAO crystal has zero second order susceptibility coefficient.

4. Conclusion

β-alanine oxalate crystals were grown from aqueous solution by slow evaporation technique at room temperature. The X-ray diffraction studies confirm the monoclinic structure of the grown crystals. The FTIR analysis confirms the presence of various functional groups. The near zero transmittance below the cut off wavelength and the high degree of transparency illustrates the optical quality of the grown samples. As seen in the spectrum, there is no significant absorption in the range 250 nm -

1100 nm. Thermal behavior of the BAO sample was studied by employing TGA, DTA and DSC analysis. The hardness study reveals that BAO crystal can only withstand low loads and at higher loads, it can break and damage and it proves that BAO crystal is a soft material. The present result shows that the grown BAO crystal does not emit green light when the light from Nd:YAG laser is passed onto the sample.

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