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RESEARCH ARTICLE

GROWTH AND CHARACTERIZATION OF A NOVEL BIS β-ALANINE PICRATE (BBAP) SINGLE CRYSTAL

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ABSTRACT

In this work, the amino acid family material viz. Bis β-Alanine Picrate(BBAP) was synthesized and single crystals of the synthesized bis β-alanine picrate were grown by adopting slow evaporation technique. The crystals are yellow in color and are transparent. The grown crystals were subjected to various characterization techniques such as X-ray diffraction analysis, FTIR analysis and TG / DTA analyses, SHG studies, UV-vis transmittance studies etc. The crystal structure of the grown crystals was found to be orthorhombic. By FTIR spectral analysis, the functional groups present in the compound have been identified. Thermal analysis was carried out to ascertain the thermal stability and mechanical strength was analyzed by measuring microhardness of the grown BBAP crystals.

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 information (Misoguti *et al.,* 1996; Manivannan and Dhanuskodi, 2004). 3-Aminopropionic acid is commonly known as β-alanine with molecular formula $C_3H_7NO_2$ and in which the amino group is at the β-position from the carboxylate group (ie. amino group is attached to the third carbon atom). 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 (Subha Nandhini *et al.,* 2002). It forms crystalline complexes with organic and inorganic acids or materials (Godzisz *et al.,* 2003). 2,4,6 –Trinitrophenol is commonly known as picric acid with molecular formula $C_6H_3N_3O_7$ and it is one of the acidic phenols. It used in dyeing industry and it crystallizes in a non-centrosymmetric space group $PCa2_1$. Picric acid forms stable picrates with various organic

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molecules through H-bonding or ionic bonding (Yamaguchi *et al.,* 1988). Researchers have been attracted to carry out the investigations on many amino acid picrates recently. Crystal growth from solution is an important process that is used to understand many physical phenomena and in this work, beta-alanine (β-alanine) was used as the base material to form a crystal with picric acid by solution method. The aim of this paper is to report the synthesis and growth of a novel Bis β-Alanine Picrate (BBAP) crystal by solution method with slow evaporation technique and to report the results of various characterization techniques adopted to study the grown crystals.

MATERIALS AND METHODS

Growth of crystal

β-alanine and picric acid were taken in the molar ratio of 2: 1 and the calculated amounts of β-alanine and picric acid were dissolved thoroughly in de-ionized water. The solution was heated at 45 ^{o}C to synthesize the BBAP salt. Re-crystallization was carried out two times to eliminate any impurities in the BBAP sample. The re-crystallized salt was used for the preparation of saturated solution and the solution was filtered using Whatman filter paper. After filtration, the solution was transferred into a beaker and the crystallization was allowed to take place at room temperature using the submerged seed solution growth technique. The crystals are transparent, free from inclusions and non-hygroscopic. Good yellow colored, transparent single crystals were obtained after 15-20 days. The grown crystal of BBAP is shown in the Figure 1. The size of the grown crystal is observed to be 16 mm x 22 mm x10 mm. The morphology of the grown crystals seems to be polyhedron in shape.

Instrumentation

Powder X-ray diffractogram for powdered sample has been recorded using a powder X-ray diffractometer (PAN alytical Model, Nickel filtered Cu K_{α} radiations(λ= 1.54056 Å) at 35 KV, 10 mA) to identify the crystal planes. The sample was scanned over the required values of 2Θ in the range 10–60 ^{o}. The grown BBAP crystal was subjected to single crystal XRD method to estimate the lattice parameters by employing Bruker-Nonious MACH3/CAD4 single X-ray diffractometer with MoK_{α} radiation (λ=0.71073 Å). The optical transmission spectrum of the sample has been recorded in the region 190-1100 nm using a Perkin Elmer UV-vis-NIR spectrometer (Model:Lambda 35). For this study, the optically polished single crysta of thickness 2 mm was used. TG/DTA studies have been carried out using STD Q600 V8.3 Build 101 -thermal analyzer at a heating rate of 20 ^{o}C / min under nitrogen atmosphere in the temperature range 30 - 800º C.

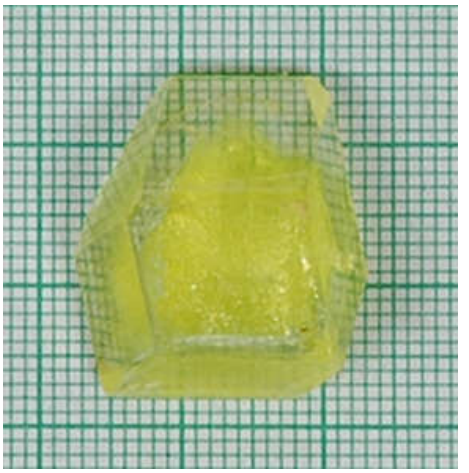

Fig. 1. The grown bis- β-alanine picrate crystal

The Second Harmonic Generation (SHG) was tested using a set-up of Kurtz and Perry (1968) and it was carried out using Q-switched mode locked Nd:YAG laser with first harmonic output at 1064 nm. Vickers hardness measurements were carried out on the BBAP crystal using ultra microhardness tester fitted with a diamond indentor. Several trials of measurements were made on the prominent face and the average diagonal length was calculated for indentation of 5 seconds. The Vickers micro hardness 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 (Kishan Rao *et al.,* 2002; Selvarajan *et al.,* 2009).

RESULTS AND DISCUSSION

XRD analysis

The powder XRD pattern for the powdered sample of DBAP crystal is shown in the Figure 2. Powder X-ray diffraction analysis has been carried out to confirm the singe crystallinity and also to identify the reflection planes and lattice parameters. All the reflections of powder XRD patterns of this work were indexed using the TREOR and INDEXING software packages following the procedure of Lipson and Steeple (1970). The values of 2θhkl values and d-values etc are presented in the Table 1. The lattice parameters were obtained from the data of powder XRD pattern using UNITCELL software package and the values are found to be a = 6.945 Å, b = 7.962 Å, c = 12.919 Å, α = 90°, β= 90°, γ= 90°. The grown single crystal of BBAP was subjected to single crystal XRD studies and the obtained single crystal XRD data are a = 6.941(1) Å, b = 7.961(3) Å, c = 12.921(2) Å, α = 90°, β= 90°, γ= 90° and V = 723.65 Å^3. From the data, it is observed that the grown crystal crystallizes in orthorhombic structure. It is noticed that the lattice parameters obtained from single crystal XRD studies are found to be in close agreement with XRD data obtained from powder XRD studies.

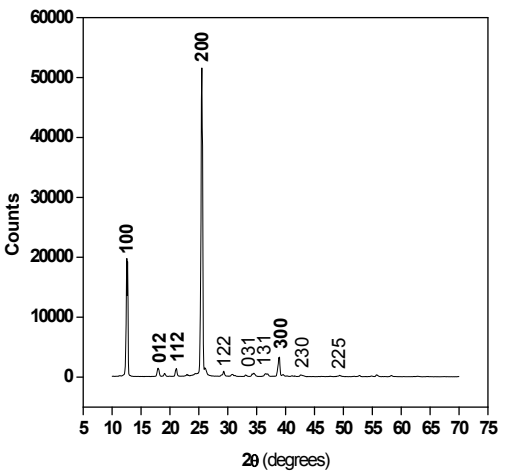

Fig.2. Powder X-ray diffraction pattern for BBAP crystal

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

2θ	d (cal)	d (obs)	h	k	l
12.62367	6.941	7.00639	1	0	0
17.96416	5.0165	4.93372	0	1	2
19.07463	4.7290	4.64892	1	0	2
21.06504	4.0658	4.21393	1	1	2
22.97658	3.98050	3.86749	0	2	0
24.35615	3.65968	3.65147	1	0	3
25.56317	3.47050	3.48173	2	0	0
29.31050	3.0453	3.04456	1	2	2
30.79861	2.92326	2.90076	0	2	3
31.29509	2.85407	2.85586	2	1	2
33.09019	2.70237	2.70492	2	0	3
34.19655	2.61586	2.61990	2	2	0
34.55179	2.59941	2.59377	0	3	1
36.46433	2.45795	2.46200	0	1	5
36.94787	2.4343	2.43088	1	3	1
38.91821	2.31367	2.31222	3	0	0
39.55350	2.27744	2.27654	3	0	1
40.28264	2023580	2.23700	2	2	3
41.63974	2.16748	2.16717	0	2	5
42.58674	2.10803	2.12115	2	3	0
46.14218	1.9665	1.96564	1	3	4
47.84271	1.90204	1.89966	0	4	2
49.35665	1.83840	1.84488	2	2	5
51.90464	1.76537	1.76014	2	3	4
52.82534	1.73525	1.73161	4	0	0
54.82042	1.67585	1.67322	4	0	2
55.73798	1.6454	1.64783	1	4	4

FTIR spectral studies

Fourier Transform Infrared spectrometry (FTIR) involves examination of the twisting, bending, rotating and vibrational modes of atoms in a molecule. Upon interaction with infrared radiation, portions of the incident radiation are absorbed at specific wavelengths and the functional groups of a sample can be identified from the spectrum. The FTIR spectrum for the grown BBAP crystal is presented in the figure 3. The CH_2 symmetric stretching vibrations are observed at 2930.63 cm^{-1}. The CN symmetric stretching vibrations are observed at 943.13 cm$^{-1.}$. CC and CH stretching are observed at 844.76 cm^{-1} .The presence of torsion oscillation of NH_3^+ is evident from the peak at 534.25 cm^{-1} . Strong band at 1261.36 cm$^{-1.}$ in the FTIR spectrum could be assigned to NH_3^+ rocking vibration. Methylene vibration is observed in FTIR in 1448.44 cm^{-1} . NH_3^+ stretching is due to vibration at the broad peak in the range 3100-2600 cm$^{-1.}$ In this figure it is observed that NO_2 symmetric stretching (υ) at 1332.72 cm^{-1} and also

in 1332.72 cm^{-1}. The phenolic O vibration produces peak at 1156 $cm^{-1.}$ Also it reveals that picric acid necessarily promotes the carboxyl group. There is N-H bending at 1663.59 $cm^{-1.}$ and asymmetric stretching of COO^- at 1572.84 cm^{-1}. The absorption peaks/bands and their assignments are provided in the table 2. The functional groups of BBAP sample were identified with the help of reported data on the vibrational frequencies of amino acids and their complexes (Hung-Wen Li *et al.*, 1998; Socrates, 1980).

Table 2. Observed IR band assignments for BBAP crystal

Wave number (cm^{-1})	*Band assignments*
534.25 (m)	NH_3^+ torision
844.76(w)	CN Stretch; CC Stretch
943.13(m)	CN Sym. Stretch
885.27(m)	CC Stretch
1059.81(s)	CN Sym, Stretch
1156.25(m)	NH_3^+ rocking
1261.36(s)	NH_3^+ rocking
1293.18(s)	CH_2 Twisting
1332.72(vs)	CH_2 wagging
1387.69(vs)	CH_2 Deformation
1413.72(vs)	COO^- Sym. Stretch
1448.44	CH_2 Scissoring
1572.84(vs)	NH_3^+ Sym. Deformation
2930.63(s)	CH_2 Sym. stretch
3120.12 (s)	NH_3^+ sym. stretch

m- medium, s-strong, vs – very strong, w- weak

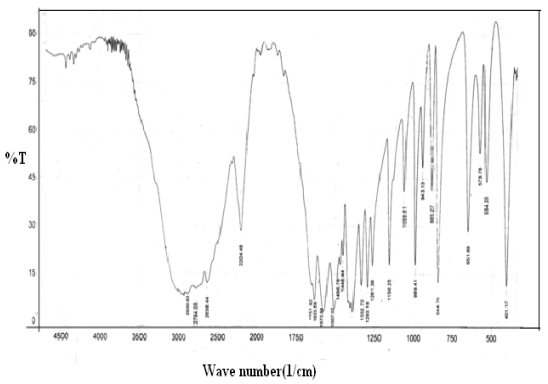

Fig.3. FTIR spectrum for the grown crystal of this work

Thermal and NLO characterization

Thermo gravimetric/Differential thermal analyses (TG/DTA) were carried out on the BBAP sample to look for possible phase transition and to determine the decomposition point. The TG/DTA response curves of BBAP are shown in fig. 4. The DTA curve shows a major endothermic peak, which corresponds to the decomposition point of the material at 228.8º C. In TGA trace, there is a major weight loss of 40% starting at about 201.8 ºC and ending at 261.34 ºC. The next weight loss of about 38% occurs between 261.34 ºC and 355.78 ºC and it shows that the decomposition is almost complete. There is one more weight loss between 335.78º and 810º C and this is due to the decomposition of the residue that is left over after the major weight loss.

In order to confirm Nonlinear Optical (NLO) property, microcrystalline form of BBAP crystal was packed separately between two transparent glass slides (sample cell). A fundamental laser beam of 1064 nm from a Nd: YAG laser was made to fall on the sample cell. Since there was no emission of green light from the sample, the Second Harmonic Generation (SHG) was not confirmed for the sample.

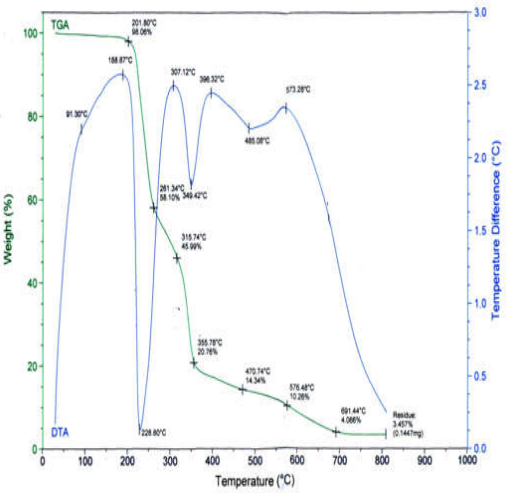

Fig. 4. TG/DTA thermograms for BBAP crystal

Mechanical characterization

Mechanical property of BBAP sample was studied by measuring microhardness number with various loads. The hardness of a material is a measure of its resistance to plastic deformation. The permanent deformation can be achieved by indentation, bending, scratching or cutting. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed. This is due to normal indentation size effect (ISE) as reported in the literature (Sivasankari and Selvarajan, 2010; Theresita Shanthi *et al.,* 2009). Figure 5 shows the variation of hardness number with different loads for the grown BBAP crystal and it is noticed that Vickers hardness number(H_v) increases with the applied load up to 100 g and cracks start developing beyond 100 g around the indentation mark. Since BBAP is a fairly soluble compound in water, it is expected to be a soft material and is evident from the microhardness test.

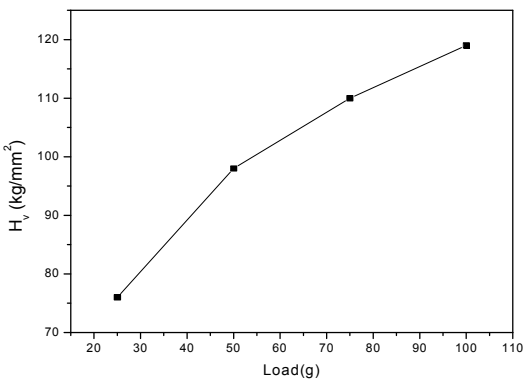

Fig. 5. Variation of microhardness number (H_v) with the applied load

UV-vis-NIR spectral studies

In order to determine the optical band gap of the grown crystal, UV–vis–NIR spectrum was recorded using an FTIR spectrophotometer. Fig. 6 shows the transmittance spectrum recorded in the wavelength range of 200-1000 nm. At about 243 nm, a sharp fall in the transmittance to zero is observed for the sample and the crystal has sufficient transmission in the entire visible and near IR region. The sharp fall at 243 nm for l the sample corresponds to fundamental absorption edge which is essential in connection with the theory of electronic structure (Krishnan *et al.,* 2008).

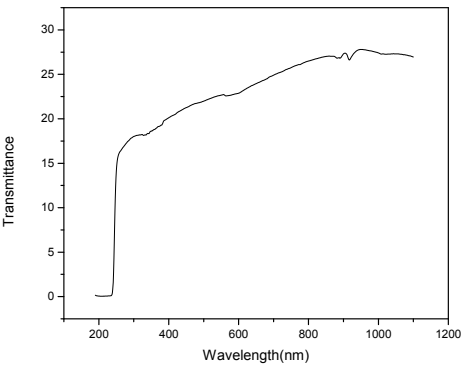

Fig. 6. UV-vis-NIR transmittance spectrum for the grown BBAP crystal

Conclusion

Semi-transparent, yellow coloured single crystals of bis-β-alanine picrate(BBAP) were grown by solution method with slow evaporation technique. Powder and single crystal XRD studies confirms the crystal structure of BBAP crystal to be orthorhombic. FTTR spectrum reveals the mode of vibrations of different molecular groups present in the title compound. Thermal analysis reveals that the BBAP crystal is stable up to 188.87 ° C. NLO studies confirm that there is no emission of green light when the fundamental laser beam of 1064 nm from a Nd: YAG laser is made to fall on the BBAP sample. The cut-off wavelength of the grown BBAP crystal is found to be 243 nm from UV-visible-NIR spectral studies.

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