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Review

Growth and Characterization of Bis-L-alanine Picrate (BLAP) Single Crystals

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Abstract

Bis L-alanine Picrate(BLAP) salt was synthesized and single crystals of BLAP were grown by solution method with slow evaporation technique. Initially, the synthesized salt was subjected to solubility studies and in accordance with the solubility data, the aqueous saturated solution of the synthesized salt was prepared at room temperature for the growth of crystals. Transparent, light-yellow coloured crystals were harvested after a period of 30 days. The grown BLAP crystals were subjected to various studies for the characterization. The crystal structure of the grown crystal was identified by single crystal and powder X-ray Diffraction(XRD) studies. FTIR Study reveals that the functional groups present in the crystal. Its optical properties were examined by UV-Vis-NIR analysis. The Vickers micro hardness values were measured for the grown crystal. SHG generation study was carried out to confirm the NLO activity of grown sample.

Keywords: Optical crystals; Crystal Growth; Single crystal; Characterization; XRD; FTIR; Microhardness

Introduction

L-Alanine [1] is an α-amino acid with the chemical formula CH_3CHNH_2COOH and is classified as non-polar amino acid. It is a white and odorless crystal powder and easily dissolves in water, slightly dissolves in alcohol and undissolves in ether. L-Alanine is the smallest, naturally occurring chiral amino acid with a non-reactive hydrophobic methyl group ($-CH_3$) as a side chain and it has the zwitterionic form both in crystal and aqueous solution over a broad range of molecular properties. L-alanine was first crystallized by Bernal[2] and later by Simpson [3] and Destro et al [4] and it is the simplest acentric crystal with second harmonic generation efficiency of about one-third of that of the well known KDP[5-7]. If L-alanine is mixed with different organic, inorganic acids and salts to form novel materials, it is expected to get improved NLO properties. Some complexes of L-alanine have been recently crystallized and various studies have been investigated by many researchers [8-10]. In this work, L-alanine is mixed with picric acid to form Bis-L-alanine picrate(BLAP) and the studies on growth, solubility, NLO activity, structural, optical and mechanical properties of BLAP crystals are reported for the first time.

Experimental techniques

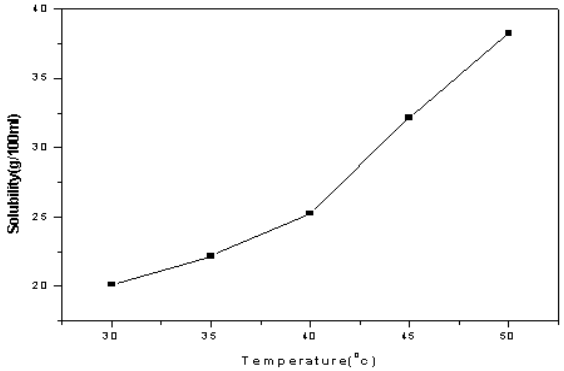
Synthesis

The title compound BLAP was synthesized by taking the chemicals such as AR grade L-alanine and picric acid in the molar ratio 2:1. The calculated amounts of the precursor chemicals were dissolved in de-ionized water and stirred well using a magnetic stirrer for about 2 hours. The solution was heated until the synthesized salt of BLAP was obtained. During the synthesis, temperature of the solution was maintained at 50 °C in order to avoid the decomposition of the sample. The purity of the synthesized salt was improved by repeated re-crystallization.

Solubility study

The solubility of BLAP in de-ionized water has been determined at five temperatures: 30 °C, 35 °C, 40 °C , 45 °C and 50 °C. Re-crystallized salt was used for these studies. Solubility of BLAP in water was determined by dissolving the solute in water in an airtight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically[11]. The solubility curve for BLAP sample is shown in figure 1. From the results, it is observed that solubility increases with temperature for the sample and the sample has positive temperature coefficient of solubility. Solubility data is necessary to prepare the saturated solution of the sample at a particular temperature.

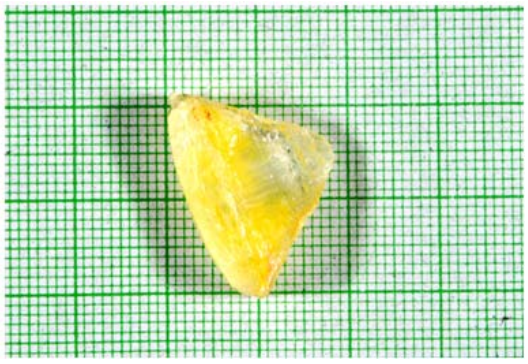
Fig.1 : Variation of solubility with temperature for BLAP sample



Growth of single crystals

Solution method with slow evaporation technique was adopted to grow the single crystals of the synthesized salt of BLAP. In accordance with the solubility data, the saturated solution was prepared and it was constantly stirred for about 2 hours using a magnetic stirrer. Then it was filtered using a 4 micro Whatmann filter paper and the filtered solution was kept in a borosil beaker covered with a porous paper. The grown crystal was harvested after a period of 30 days and it is displayed in the photograph(Fig.2). It is seen that the grown crystal is yellow in colour and shape is observed to conical.

Fig.2: The grown of BLAP single crystal



Characterization methods

Single crystal XRD data for BLAP crystal was obtained by employing Bruker-Nonious MACH3/CAD4 single X-ray diffractometer with MoK_α radiation (λ=0.71073 Å) from M.K.University, Madurai. To identify the reflection planes, powder X-ray diffraction pattern of the powdered sample was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K_α radiations

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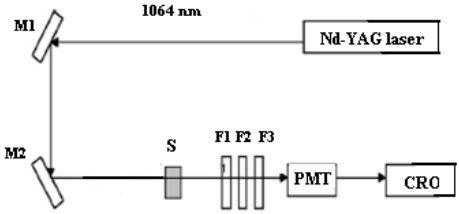
with λ= 1.54056 Å at 35 KV, 10 mA). The sample was scanned over the required range for 2Θ values(10-70 °). The powder XRD pattern of the sample was recorded at RRL, Trivandrum. The FTIR spectrum of the sample was recorded at M.K.University, Madurai using a Shimadzu 8400S spectrometer by the KBr pellet technique in the range 400-4500 cm^{-1}. The optical spectra of BLAP crystal have been recorded in the region 190-1100 nm using a Perkin Elmer (Model:Lambda 35) UV-vis-NIR spectrometer. Microhardness test was carried out at St.Joseph's College, Trichy using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study on the grown BLAP crystal. Indentations were made for various loads from 25 g to 100 g. Several trials of indentation were carried out on the (100) plane and the average diagonal lengths were measured for an indentation time of 10 seconds. The Vickers micro hardness number was calculated using the relation $H_v = 1.8544\ P / d^2$ kg/mm^2 where *P* is the applied load and *d* is the diagonal length of the indentation impression[12,13].

The Second Harmonic Generation(SHG) efficiency for the sample was measured at Crescent Engineering College, Chennai by Kurtz-Perry powder technique[14] . The BLAP crystal was powdered with uniform particle size using a ball mill and it was packed densely between two transparent glass slides. An Nd:YAG laser was used as a light source. This laser device can be operated in two different-modes. In the single-shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulse at a repetition rate of 10 Hz. In the present study, a multi-shot mode of 8 ns laser pulse with a spot radius of 1mm was used. The experimental set-up for measuring SHG efficiency is shown in the figure 3. The fundamental laser beam of 1064 nm wavelength, 8 ns pulse with 10 Hz pulse rate was made to fall normally on the sample cell(S). The power of the incident beam was measured using a power meter. The filter F1 removes the 1064 nm light and the filter F2 is a BG-38 filter, which also removes the residual 1064 nm light. F3 is an interference filter with bandwidth of 4 nm and central wavelength 532 nm. The green light was detected by a photomultiplier tube (PMT) and displayed on a Cathode Ray Oscilloscope(CRO). KDP crystal was powdered into identical size as BLAP crystal and it was used as reference material in the SHG measurement.

Fig.3: Experimental set-up for SHG measurement



Results and Discussion

Powder XRD method is useful for confirming the identity of a crystalline material and determining the phase purity. Bis L-alanine picrate(BLAP) crystal was ground into powder and it is subjected to powder X-ray diffraction studies. The powder XRD pattern of the sample is shown in figure 3. The well-defined peaks at specific 2Θ values show high crystallinity of the grown crystals. All the reflections of powder XRD patterns of this work were indexed using the INDEXING and TREOR software packages. The lattice parameters obtained from the indexed XRD patterns using UNITCELL software package are observed to be comparable with the values obtained from single crystal XRD studies and the values are tabulated in the table 1. From X-ray diffraction data, it is observed that the BLAP crystal is orthorhombic in structure with space group $P2_12_12_1$.

Fig 3:Powder XRD pattern for powdered sample of BLAP crystal

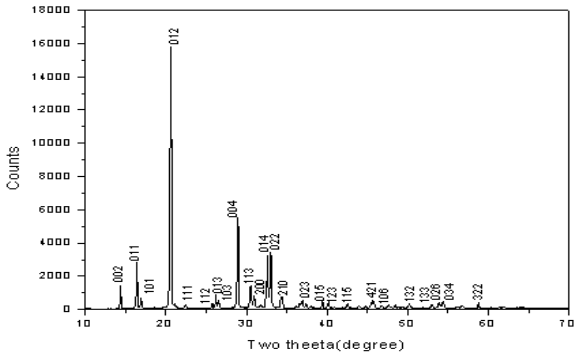


Table 1: Unit cell parameters for BLAP crystal

Sample	Cell parameters	volume
Bis L-alanine picrate(BLAP)	a=5.789(2)A^0 b=6.027(2)A^0 c= 12.337(2)A^0 α=β=γ=90^0	430.4(2) $(A^0)^3$

The FTIR spectrum of the grown BLAP crystal was recorded in the KBr phase in the frequency region 450–4500 cm^{-1} using Perkin Elmer spectrometer and is shown in figure 4. The assignments for the absorption peaks/bands are provided in accordance with the data reported in the literature [15]. The phenolic O vibration produces peak at 1154 cm^{-1} . Also, it reveals that picric acid necessarily protanates the carboxyl group. The observed absorption peaks/bands and the wave number assignments of BLAP sample are given in table 2.

Fig.4: FTIR spectrum for Bis-L-alanine picrate sample

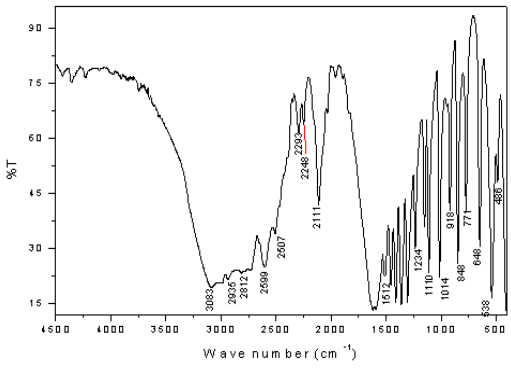


Table 2: Assignments for vibrational frequencies observed in FTIR spectra of Bis L-alanine picrate sample

Wave number(cm^{-1})	Assignments
3083	NH_3^+sym.str. and aromatic C-H
2935	CH_2 asym.str.
2812	CH str.
2599	CH str.
2293	C-O band stretching
2248	Aromatic vibration of C-N
2111	Combination band
1512	NH_3^+torsion
1234	COO^-sym.str
1154	Phenolic O
1110	NH_3+ rocking
1014	C-N str.
918	C-C-N sym.str.
848	C-C-N sym.str.
771	O-C-O deformation
648	COO^- scissoring
538	COO^- rock
486	NH_3^+torsion

In order to determine the optical transmission characteristics of the grown crystal, UV–vis–NIR spectrum was recorded using a spectrophotometer. Optically clear single crystal of thickness about 2 mm was used for this study. UV-visible absorption and transmittance spectra of bis-L-alanine picrate crystal in the wave length region 200-1100 nm are shown in figures 5 and 6. This spectral study may be assisted in understanding electronic structure of the optical band gap of the crystal. From the figures, it is observed that there is an absorption noticed at 516 nm. This is due to yellow colour of the crystal.

Fig.5: UV-visible absorption spectrum for BLAP crystal

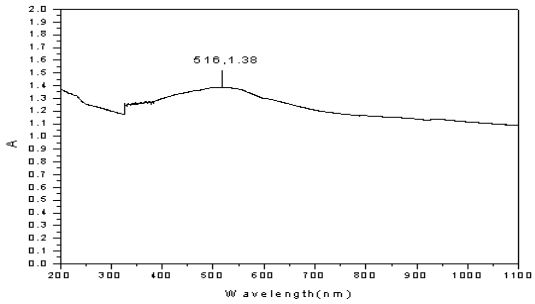
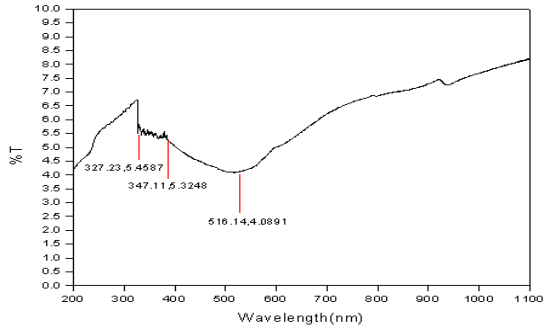


Fig.6: UV-visible transmittance spectrum for BLAP crystal



In order to confirm Nonlinear Optical(NLO) property, microcrystalline form of the grown crystal was packed between two transparent glass slides(sample cell). Second-harmonic radiation generated by the randomly oriented microcrystals was focused by a lens and detected by a photomultiplier tube after filtration of the incident or fundamental radiation of 1064 nm. The doubling of frequency was confirmed by the green color of the output radiation whose characteristic wavelength is 532 nm. The relative measured output from the specimen with respect to KDP crystal shows that SHG efficiency of the grown BLAP crystal is 0.8 times that of KDP.
Mechanical strength of a crystal was studied by measuring microhardness and it plays an important role in the fabrication of opto-electronic devices. 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)[16]. The variation of Vickers hardness number(Hv) with various loads for BLAP crystal is shown in figure 7. It was observed that microhardness number increases with increase in load upto 100 g. Further increase in load causes cracks formation which leads the decrease in hardness value. This may be due to the release of internal stress. Fig .8 shows the variation of log P with log d. The work hardening coefficient n was determined from the slope of log P versus log d plot using least square fit method. The value of n was found to be less than 2. According to theory[17], if n>2, microhardness increases with increasing load and decreases with increasing load if n<2. The increase in Hv for increasing in load observed in the present study is in good agreement with the theoretical predication.

Fig 7: Variation of Vickers hardness number with load for the BLAP crystal

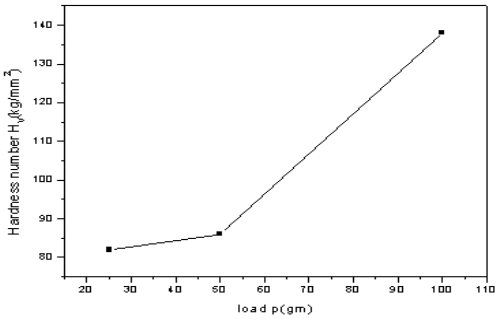
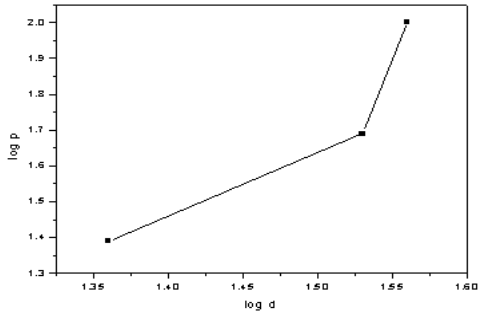


Fig 8: Variation of log P with log d for the Bis-L-alanine picrate crystal



Conclusions

BLAP salt was synthesized by solution method by mixing L-alanine and picric acid in 2:1 molar ratio. Single crystals of BLAP have been grown by slow evaporation solution growth technique. The grown crystals were transparent and yellow in colour. The solubility of BLAP sample was observed to be increasing with increase in temperature. The unit cell parameters for BLAP crystal have been found out XRD method and the crystal structure is confirmed to be orthorhombic. The spectroscopic techniques such as FTIR spectral analysis and the optical absorption studies were carried out to characterize the grown crystals. The NLO efficiency of BLAP sample is found to be 0.80 times that of KDP. The microhardness study indicates that the crystal belongs to the class of soft materials.

Acknowledgement

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