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Thermal Stability and Micro Hardness of ADP and Sulphamic Acid Admixtured Beta Alanine Single Crystals

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Abstract-- Single crystals of ADP and Sulphamic acid admixtured Beta Alanine were grown by slow evaporation solution growth method. The crystal structure was found to be tetragonal according to single crystal X-ray diffraction studies. Sharp peaks appeared in the powder X-ray diffraction pattern proved the good crystalline nature of the sample. FTIR spectral analysis revealed the possible functional groups and modes of vibration. Vicker's microhardness analysis was used to estimate the mechanical parameters of the sample like work hardening index , yield strength ,elastic stiffness constant , brittleness index and fracture toughness co-efficient of the grown crystals Especially, the thermal stability of the materials is an important parameter checked and the mechanical strength is another deciding property to be analyzed before choosing any material for fabrication purposes.TG-DTA studies done confirmed the thermal stability of the crystals.

Key words-- Solution growth, XRD analysis, FTIR spectrum, Vicker's micro hardness studies, TG-DTA graph

I. INTRODUCTION

Ammonium Dihydrogen Phosphate, which is an important isomorph of Potassium Dihydrogen Phosphate crystal, has been widely used for frequency conversion in laser systems, optical switches and acousto-optical devices. This hydrogen bonded compound also exhibits piezoelectric activity and low temperature order-disorder phase transition. Below 148.5 K, ADP is ferroelectric and belongs to $P2_12_12_1$ space symmetry group while above this temperature, it is paraelectric having I4/2d symmetry. This is also nonlinear optical material having applications in the field of photonics for frequency mixing, parametric amplification and electro optic modulation. As a new attempt, β alanine, ADP and sulphamic acid are taken in calculated proportions to grow a novel NLO single crystal which is identified in this work as BADSA. These newly grown single crystals are later found to posses second harmonic generation efficiency greater than ADP. To avail the maximum usage of these crystals, different properties of these crystals were analyzed by the corresponding characterization tools and presented in this paper.

II. METHOD OF CRYSTAL GROWTH

Analar Reagent (AR) grade chemicals Ammonium Dihydrogen Orthophosphate (ADP) and sulphamic acid were purchased commercially to grow BADSA crystal. Here β-alanine and ADP are taken in the molar ratio 1:1. With this, 1mole % of sulphamic acid was added to yield NLO single crystal BADSA and dissolved in double distilled water The solution was stirred well using a magnetic stirrer for three hours and filtered [1,2]. The solution was kept undisturbed in dust free atmosphere till transparent colourless single crystals BADSA were harvested after a period of 14 days. The photograph of the crystals is shown in fig. 1.

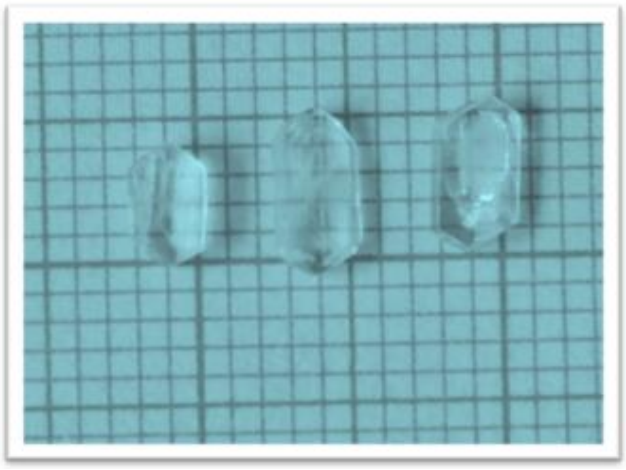

Figure 1: Photograph of harvested BADSA crystal

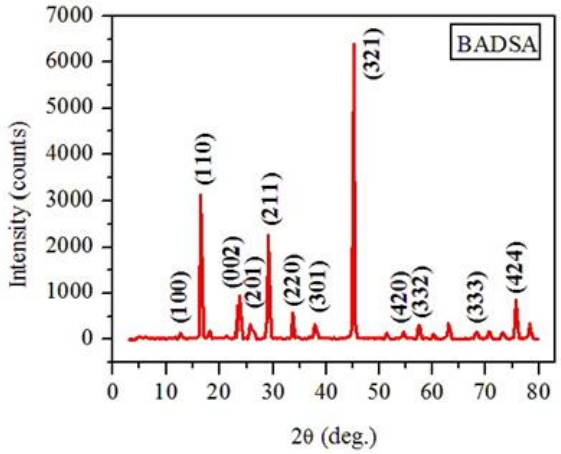

Figure 2: Powder X-ray diffraction pattern of crystal BADSA

III. RESULTS AND DISCUSSION

A. Single crystal X-ray diffraction analysis

The unit cell parameters and crystalline system of these crystals BADSA were found out using BRUKER- NONIUS MACH3 /CAD4 single crystal X-ray diffractometer and tabulated in table 1.

Table 1: Cell parameter values of BADSA single crystals

Sample	System	a(Å)	b(Å)	c(Å)	V(Å)^3
BADSA	Tetragonal	7.53	7.53	7.61	431

B. Powder X-ray diffraction analysis

The harvested crystals BADSA were ground into fine powder and the powder X-ray diffractions were recorded using X-ray diffractometer using BRUKER AXS D8 advance diffractometer with CuK_α (λ=1.5418 Å) radiation . The sample was scanned over the range 0-80 ^{o} at the rate of 2 per minute. The crystalline phase structure of the samples was identified from the crystallographic parameters such as 2θ, d-spacing, relative intensity and hkl values. From the patterns 2θ values were read directly and the relative intensity of the diffraction peaks can be estimated. The d-spacings corresponding to different peak positions were calculated using Bragg's law $2d\sin\theta = n\lambda$ where d is the interplanar spacing, θ is the angle of diffraction, n is the order of diffraction and λ is the wavelength of X-rays used. The peaks were indexed using the procedures of Lipson and Steeple. The powder X-ray diffraction spectrum for the crystals is plotted in fig. 2.

C. FTIR spectral analysis

The Fourier Transform Infrared spectral analysis has been carried out to understand the chemical bonding and it provides useful information regarding the molecular structure of the compound. The spectrum was recorded with Perkin Elmer FTIR spectrometer in 400 - 4000 cm^{-1} range using KBr pellet technique. Infrared absorption studies involve examination of stretching, bending, twisting, rotating and vibrational modes of atoms in a molecule and hence to identified the functional groups of the samples. FTIR spectrum is interpreted using known group frequencies and thus it is easier to characterize the substance.

The FTIR Spectra of the crystals is given in fig.3 and the corresponding spectral assignments are displayed in table 2.

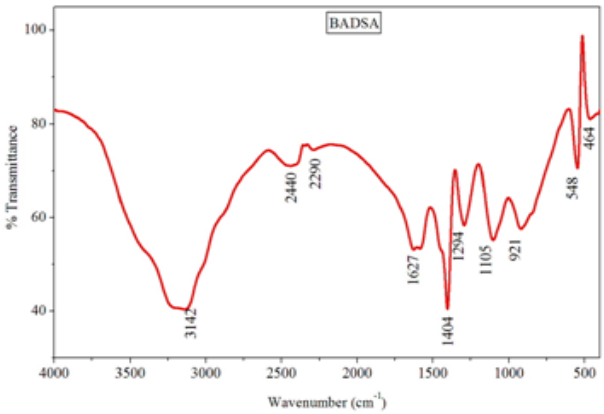

Figure 3: FTIR spectrum of BADSA

Table 2: Spectral assignments for BADSA

BADSA	
Wave number cm^{-1}	**Assignments**
3142	NH_3^+ Stretching
2440	N-H Stretching
2290	CH_3 Stretching
1627	NH_3^+ Symmetric vibrations
1404	C=S Symmetric Stretching
1294	C-O Stretching
1105	SO_3^- Stretching vibrations
921	C-C-N Symmetric Stretching
548	SO_3^- Deformation
464	COO^- wagging

D. Microhardness studies

The Vickers microhardness numbers for the grown crystals BADSA were determined using SHIMAZDU HMV-2T microhardness tester. The indentations were made on the polished crystals for the loads 25, 50 and 100 g. The indentation time was kept as 5s for all the loads. The Vickers hardness number H_v was calculated. The graph showing the variation in H_v with load is given in fig. 4. Hardness is observed to be increase in load and this is due to reverse indentation size effect. For small notes, only a few surface layers are penetrated by the indenter. Measured hardness is the characteristics of these layer and hardness increases with load in this region. But with increase in load, the overall effect is due to surface as well as inner layers of the samples. The relation between load and the size of the indentation is given by Meyer's law

$$P = ad^n$$

Where a and n are constants of the material. The plot of logP and log d is shown in fig .5. The slope of the plot gives the work hardening coefficient (n)[3]. The values of n estimated for these three crystals are given in table 3.

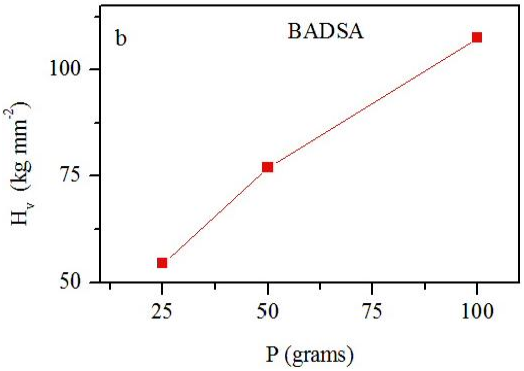

Figure 4: Variation of Vicker's hardness number (H_V) with load (P)

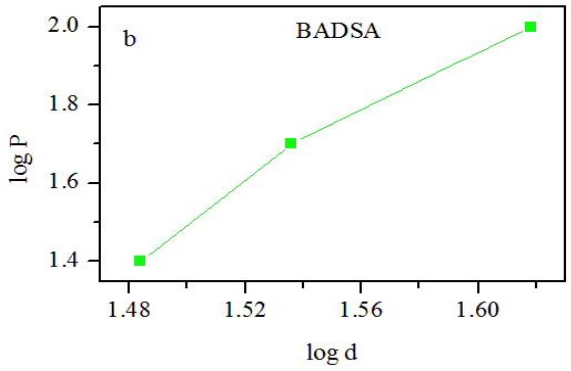

Figure 5: Graph between log d and log P

Table 3: Work hardening coefficient of the grown crystals

Sample	N
BADSA	4.404

Other mechanical parameters of the crystals are calculated and tabulated in table 6. Since yield strength, elastic stiffness constant and fracture toughness coefficient increase with load, these crystals have tightness in bonding and have high mechanical strength [4]. So the crystals can be recommended for device fabrication[5]. The variation in mechanical parameters with load is plotted in fig.6.

Table 4: Mechanical parameters of BADSA

Load (P) gm	Yield strength (σ_y) MPa	Elastic stiffness constant (C_{11}) 10^{14} Pa	Fracture toughness (K_c) 10^5 kgm$^{-3/2}$	Brittleness index (B) m$^{-1/2}$
25	1.306	18.644	1.408	385.79
50	1.852	34.356	2.815	273.54
100	2.585	61.604	5.630	190.94

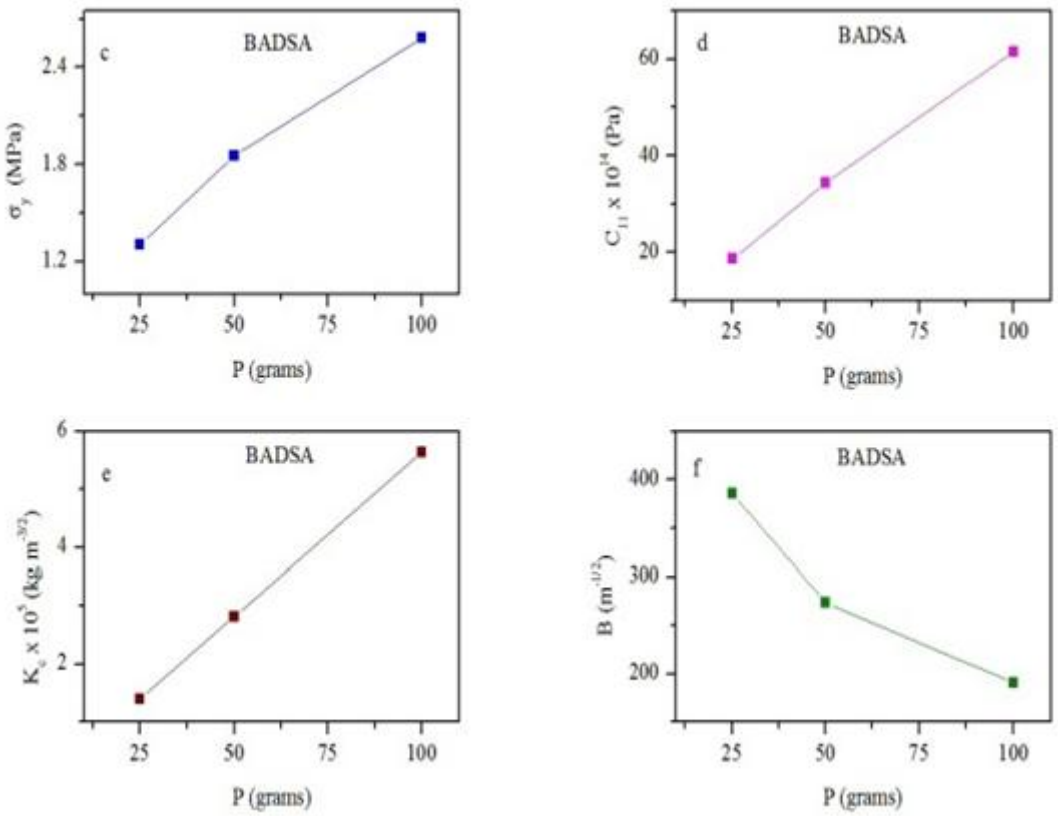

Figure 6: Plot of Mechanical Parameters with Load

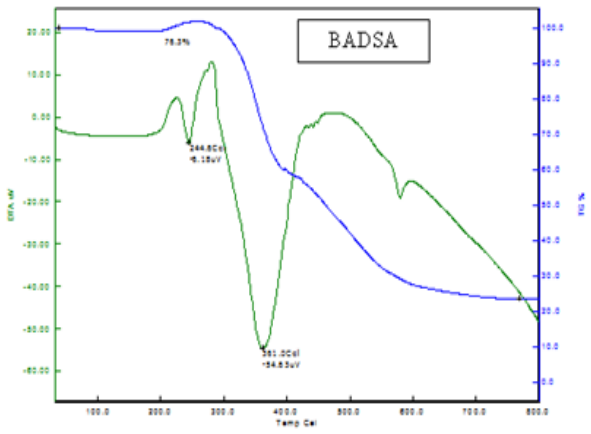

Figure 7: TG - DTA curve for the crystal BADSA

E. Thermal analysis

Studies of thermogravimetric and differential thermal analysis (TG-DTA) were carried out using Perkin Elmer Diamond Instrument in Nitrogen atmosphere to check the thermal stability and to identify various endothermic and exothermic transitions [6]. The thermal curve of the grown crystals BADSA is given in fig.7.

In BADSA, the thermal stability is seen upto temperature 210 ^oC. There is a small endothermic peak seen at 244 ^oC which may account for the beginning of decomposition. The melting point of the crystal is 371 ^oC which is inferred from the sharp endothermic peak. In TG, a weight loss of 76.3 % is noticed between the temperature 300 ^oC and 550 ^oC. The high thermal stability of BADSA recommends its usage in various applications and device fabrication [7, 8].

CONCLUSION

Novel single crystals BADSA were grown successfully using slow evaporation solution growth method. The crystalline nature and lattice parameters were found out using single crystal XRD analysis. Powder XRD pattern of the crystals were obtained and the reflecting planes were indexed. The possible functional groups present in the crystals were determined from FTIR spectra. The hardness studies revealed

the mechanical strength of the crystals. Thermal stability of the sample was checked using TG-DTA analysis.

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