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Studies on Growth, Structural, Mechanical and Optical Properties of Beta Alanine Thiourea Oxalate – An Nlo Single Crystal

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Abstract: *Single crystals of Beta Alanine Thiourea Oxalate (BATO) were grown by slow evaporation solution growth method. The crystal structure was found to be monoclinic 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. Optical parameters such as refractive index , extinction co-efficient , optical absorption co-efficient , optical conductivity , electrical conductivity and electrical susceptibility of the grown crystal were calculated from UV-Vis-NIR spectral studies. 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 . SHG efficiency of the crystal was checked using Kurtz Perry powder technique.*

Key Words: *Solution growth, XRD analysis, FTIR spectrum, SHG , Vicker's microhardness , UV-VIS Spectral analysis*

I. Introduction

Potential applications of NLO materials in the fields of communication and electronics have recently developed an unquenchable thirst among the researchers to grow novel NLO single crystals with highly desired properties. Eventhough organic materials have high degree of delocalization and more optical nonlinearity, in order to achieve hybrid materials which posses high melting point, high mechanical strength and chemical inertness, they have to be combined with inorganic materials. These hybrid materials have remarkable optical nonlinearity, wider transmittance in the visible region, high thermal stability and higher laser threshold. [1]-[3].Thiourea ,being an interesting inorganic matrix modifier because of its large dipole moment, has also the stability to form extensive network of hydrogen bond and the co-ordination capacity to form new complexes.[4] Several NLO crystals have been grown using thiourea. [5]-[6] As a new attempt, it is here combined with both an aminoacid and a carboxylic acid.

II. Experimental Work

AR Grade chemicals β-alanine, thiourea and oxalic acid were purchased and the calculated amount were taken in equimolar ratio. Deionised water and temperature controlled magnetic stirrer were used to prepare highly homogeneous uniform mixture of the solution. After a series of filteration and repeated recrystallization, the solution was kept undisturbed in dustfree atmosphere. Colourless optically transparent single crystals of BATO shown in fig.1 were harvested after a period of 15 days using slow evoporation technique.

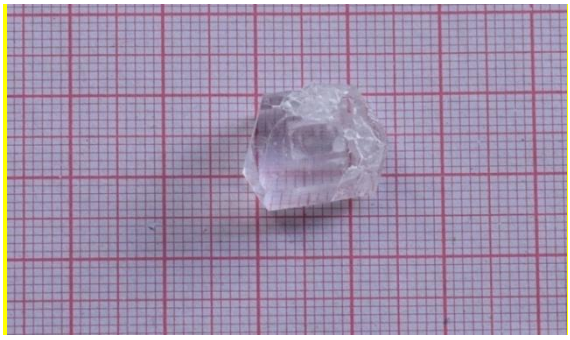

Fig.1. Photograph of the crystal.

III. Results And Discussion

3.1. Single Crystal X-RAY Diffraction Analysis

The structure of the grown BATO single cystal was analyzed using Bruker-Nonius MACH3/CAD4 single crystal X-ray diffractometer. From the data , it was observed that the grown crystal belongs to monoclinic structure with lattice parameters a=22.325A^{o} , b=5.6795A^{o} , C=14.001A^{o}, $\alpha = \Upsilon = 90^{o}$, $\beta = 115.12^{o}$ and volume=1607.5(A^{o})^{3}

3.2. Powder X-RAY Diffraction Analysis

Powder X-Ray diffraction pattern was recorded using BRUKER AXS D8 advance diffractometer with CuKα (λ=1.5418A0) radiation after crushing the sample into fine powder.The sample was scanned over the range 10-100 degree at the rate of 2 degree per minute.The powder XRD pattern obtained is shown in the fig.2.It was indexed using least square fit method to identify the reflecting planes .The sharp and well defined peaks at specific 2θ values testify the excellent crystalline nature and purity of the grown crystal. Crystalline size was estimated using Scherrer formula

$$D=K\lambda/\beta COS\theta$$

and it lies in the nanoregion(24nm- 74nm).

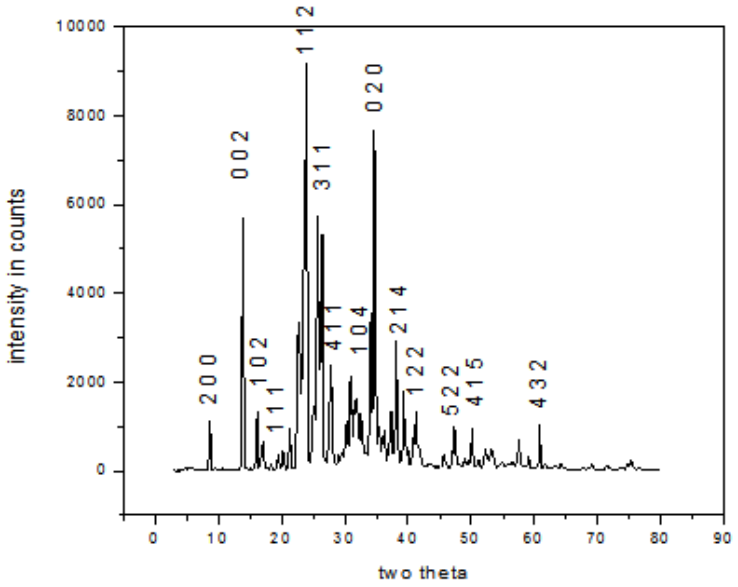

Fig. 2. PXRD Pattern

3.3.FTIR Spectral Analysis

Freshly crushed powder of BATO was mixed with KBr in the ratio 1:10 and pelletized using a hydraulic press and subjected to Fourier Transform Infrared Spectral studies. The spectrum given in fig. 3 was recorded in the range 400-4000cm^{-1} employing BRUKER IFS 66V FT-IR Spectrometer .The N-H stretching vibrations of amino group are found at 1526 , 1402 and 1024cm^{-1}. The absorption at 3085cm^{-1} is due to O-H stretching vibrations of carboxylic group. The strong absorption at 1713cm^{-1} indicates the existence of carbonyl stretching vibration. N-H bending vibrations gives the peak at 1617cm^{-1}. C-N stretching vibrations and NH_2 rocking vibrations appear at 1203 and 1124cm^{-1} respectively.The peaks at 801 and 701 cm^{-1} indicate the existence of NH_2 wagging and CH out of plane bending vibrations respectively. N-C-N stretching vibrations due to thiourea gives the peak at 478 cm^{-1}[7]-[11].

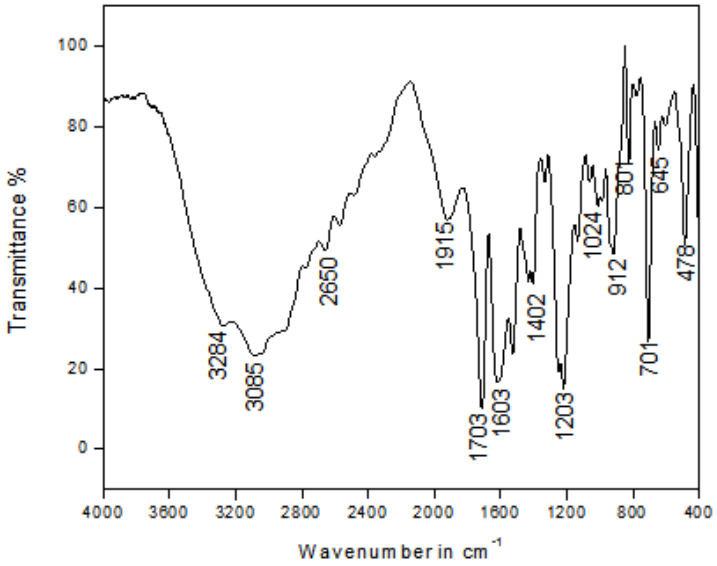

Fig.3. FTIR Spectrum

3.4.UV-VIS-NIR Spectral Analysis

3.4.1 optical trasmission studies

Optical transmission spectrum of BATO single crystal was recorded using Lambda 35 spectrophotometer in the wavelength region 400 - 1100nm and is shown in fig .4.

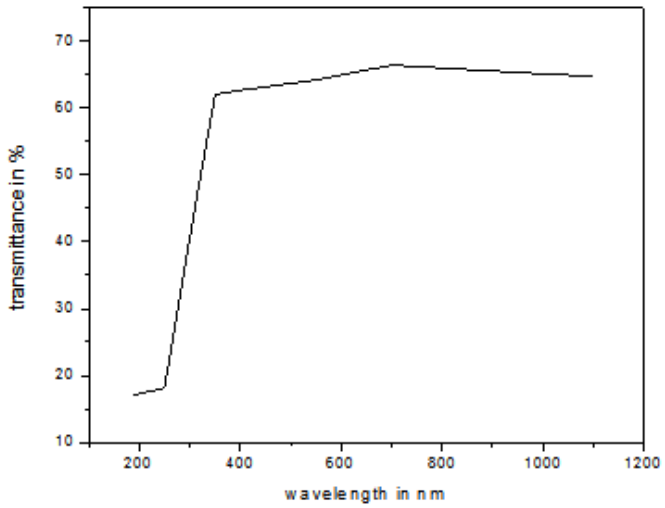

Fig.4. UV-Visible Spectrum

For optical device fabrications , the crystal should be highly transparent in a wide region of wavelength and it should have remarkable value of transmittance in the entire visible region.[12].From the figure, UV absorption edge of the grown crystal was observed to be around 220 nm. Fig.5 shows how the absorbance in the crystal varies with wavelength. The absorbance is found to be low in the visible region and IR region due to delocalization of electron cloud through charge transfer axis which is the most desirable property of NLO materials.

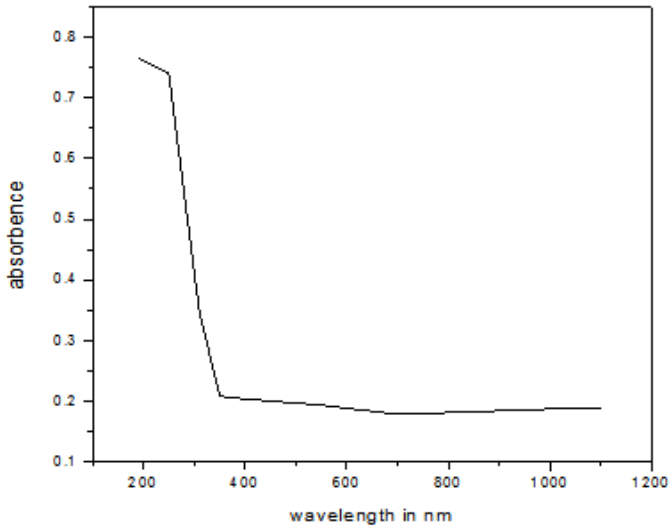

Fig.5. Absorbance versus wavelength

Optical absorption co-efficient (α) was calculated from transmittance using the relation

$$\alpha = \frac{2.303 \log\ [\frac{1}{T}]}{t}$$

w here T is the trasmittance and t , the thickness of the crystal. Moreover, the dependence of optical absorption co-efficient on photon energy helps to study the band structure and type of transition of the electrons. The relation between optical absorption co-efficient and wavelength is shown in fig.6.

For a direct band gap material, the crystal under study has an absorption co-efficient(α) obeying the following relation for high photon energies,

$$\alpha = \frac{A\sqrt{[h\nu - Eg]}}{h\nu}$$

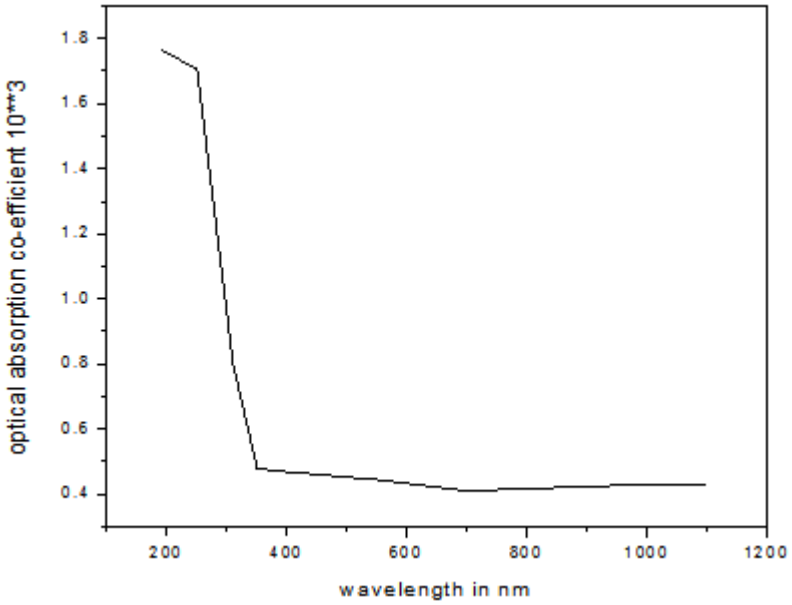

Fig.6. Opticalabsorption co-efficient versus wavelength

Where Eg is the optical bandgap of the crystal and A is a constant . Tauc's plot (i.e) $(\alpha h\nu)^2$ versus hν is shown in fig. 7.

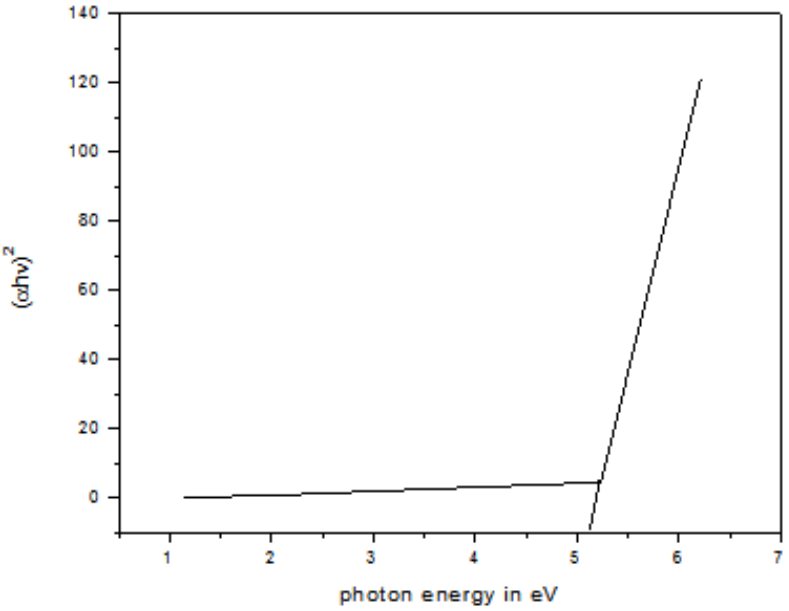

Fig.7. Tauc's Plot

Eg is evaluated by extrapolating the linear part of the curve and the band gap energy is found to be 5.15 eV .As a consequence of wide bandgap , the crystal has large transmittance in the visible region.

3.4.2 Determination of optical constants

Optical behaviour of the crystal is important in the process of fabricating optoelectronic devices. Knowledge of optical constants of a material such as optical band gap, extinction co-efficient, refractive index , optical conductivity , and dielectric constant are quite essential to examine the potential applications of the crystal in the field of optoelectronics. [13]-[15].Further the optical properties are closely related to electrical properties , atomic structure and electronic band structure of the crystal. Absorbance (A)in the crystal can be evaluated using the relation

$$A = \log[\frac{1}{T}]$$

And reflectance (R)can be found out from

$$R = 1-(T+A)$$

Extinction co-efficient (K) which is the measure of amount of incident light lost due to scattering and absorption per unit distance of the sample and it can be evaluated from the relation

$$K = \frac{\alpha\lambda}{4\pi}$$

Reflectance and refractive index(n) are related as follows:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$$

Uniformity of refractive index throughout an optical element is a prime consideration in selecting materials for high performance lasers , elements for coherent optics , and acousto optical devices .

The variation of refractive index and extinction co-efficient with wavelength are given in fig 8 and 9 respectively. There is uniformity of refractive index throughout the visible region which is the desirable property for device fabrication.

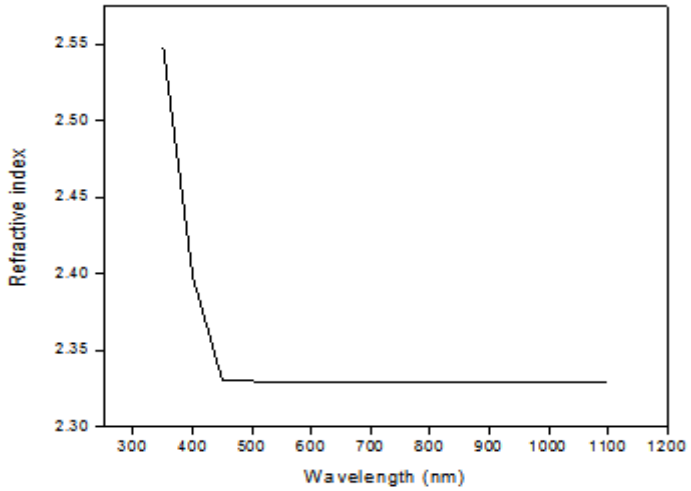

Fig.8. Variation of refractive index with wavelength

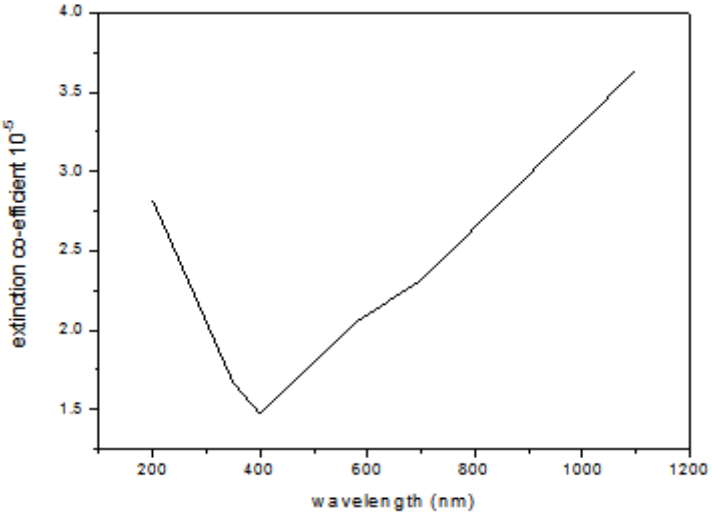

Fig.9. Dependance of extinction co-efficient with wavelength

The relation between optical conductivity and electrical conductivity with wavelength is shown in the fig.10 ,11 respectively. Optical conductivity is a measure of frequency response of the material when irradiated with light and electrical conductivity tells about the behavior of charge carriers in the exposure of light.

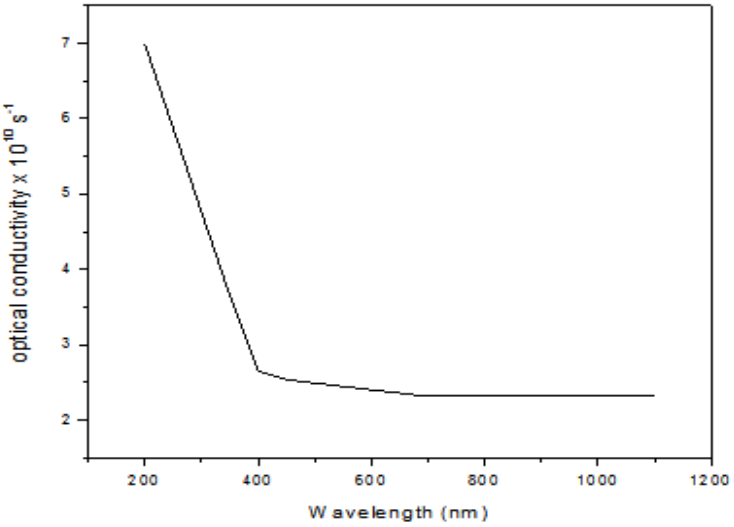

Fig.10. Variation of optical conductivity with wavelength

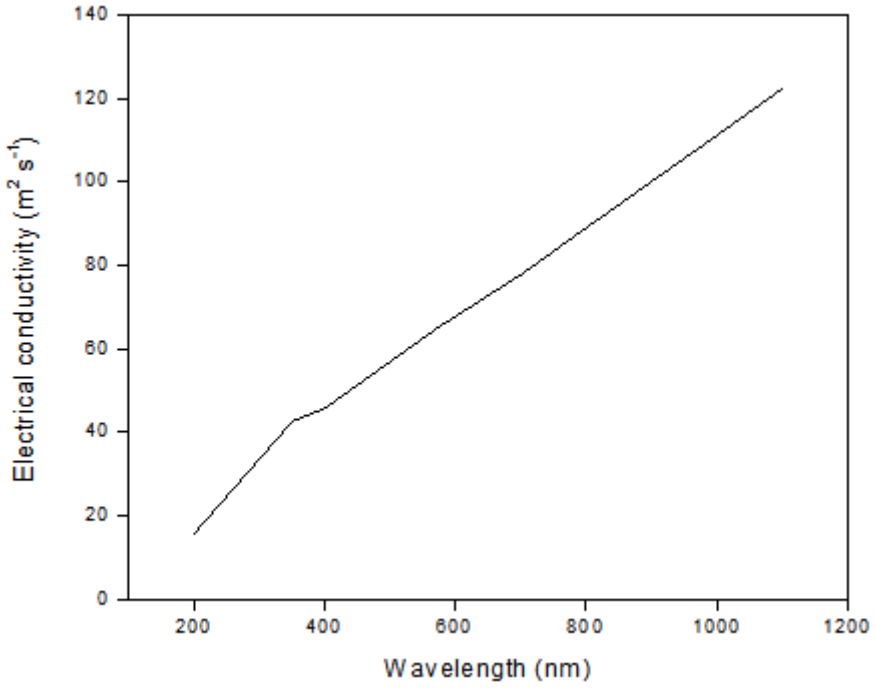

Fig.11. Electrical conductivity versus wavelength

By examining all these curves, one can get complete knowledge regarding the choice of material for the fabrication of electro optic and opto electronic devices.

Electric susceptibility(χ_c) and real and imaginary parts of dielectric constant(ε_r, ε_i) are calculated with the help of the following relations

$$\chi_c = (n^2 - k^2 - \varepsilon_0) / 4\pi$$
$$\varepsilon_r = n^2 - k^2$$
$$\varepsilon_i = 2nk$$

At wavelength 700 nm , the calculated values are

$\chi_c = 0.4318$, $\varepsilon_r = 5.424$, $\varepsilon_i = 10.797 \times 10^{-5}$

3.6.SHG Studies

Nonlinear optical property of BATO was tested by Kurtz and Perry powder technique and its efficiency was compared with that of KDP and urea. A Q -switched mode locked LASER operating at wavelength 1064nm generating 2mJ/pulse was used for the study. The emission of green radiation 532 nm from the sample confirms that the sample exhibits SHG property. Second harmonic signal obtained from the crystal was 89mV whereas microcrystalline powder of urea gave 180mV and KDP produced 150mV . Hence the SHG efficiency of the grown crystal BATO is nearly 0.59 times that of KDP and 0.49 times that of urea.

3.7. Microhardness Studies

The structure and molecular composition of the crystal greatly influence the mechanical properties. Microhardness testing is one of the simplest and best methods to understand the strength of the crystal .Hardness of the material is a measure of resistance offered by the lattice for permanent deformation.[16].Thus hardness is related to the bondstrength and plasticity of the grown crystal. Microhardness studies have been carried out on a selected well transparent single crystal using microhardness tester fitted with Vicker's diamond pyramidal indenter. The value of Vicker's microhardness(Hv) at different loads was calculated using the relation

$$H_v = 1.8544\ P/d^2\ Kg/mm^2$$

where P is the applied load in Kg and d is the mean diagonal length of the indenter impression inmm2. Variation of hardness with load is plotted in fig.12 which shows that hardness of BATO increases with load which is reverse indentation size effect.[17]

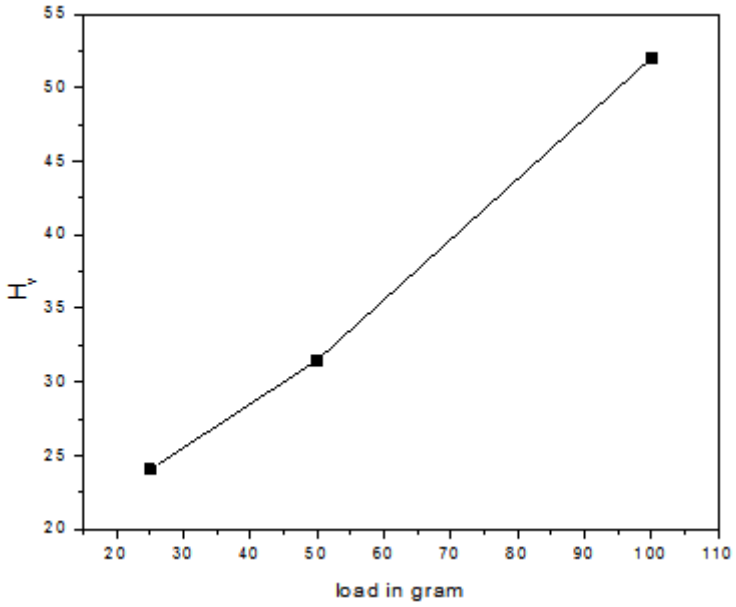

Fig.12. Hardness versus load

According to Mayer's law, the relationship between the load and the size of the indentation is given as

$$P = Kd^n$$

Where n is called Mayer index or work hardening index. Plotting a curve between log d and log P , and finding the slope as in fig.13 , we get the value of n. Since n =4.67, BATO belongs to the category of soft materials. [18]

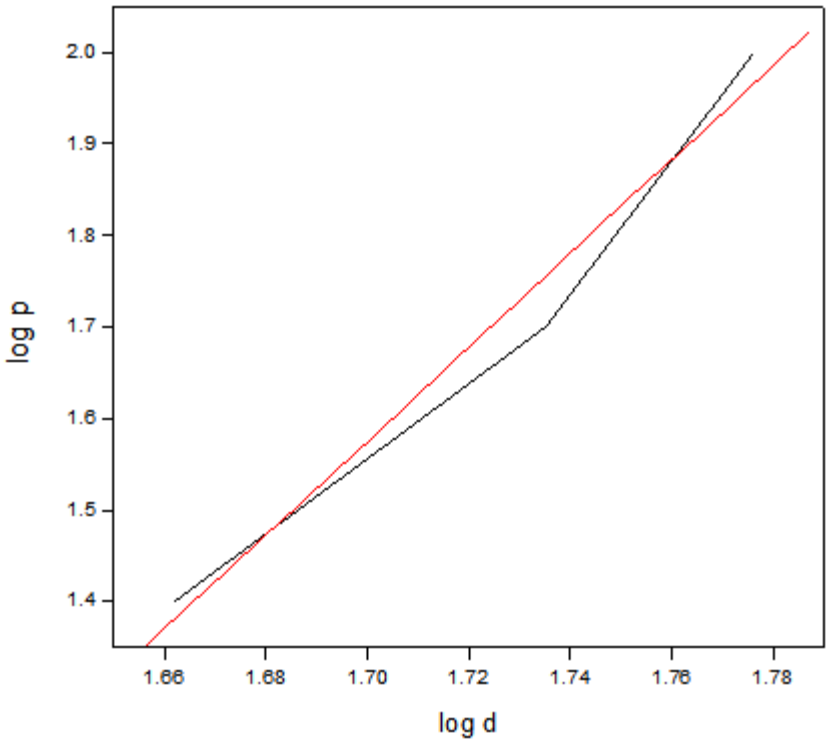

Fig.13. log P versus log d

Yield strength of the crystal (σ_y), elastic stiffness constant(C_{11}) , fracture toughness(Kc) and brittleness index(B)[19,20] are estimated according to the following relations and tabulated in Table 1.

$$Бy = (Hv/3)(0.1)^{(n-2)}$$

$$C_{11} = (H_V)^{7/4}$$

$$Kc = P/\beta c^{3/2}$$
$$B = Hv/Kc$$

Where c is the crack length measured from the centre of the intendation mark to the crack tip and β=7 for Vicker's indenter .Since yield strength and elastic stiffness constant of the material increase with load ,BATO has high mechanical strength.

Table 1. Mechanical parameters of grown crystal BATO

Load (gm)	Yield strength($Б_y$) MPa	Elastic stiffness constant(C_{11})10^{14} Pa	Fracture toughness (K_c) 10^4 $Kgm^{-3/2}$	Brittleness index (B) 10^{-8} $m^{-1/2}$
25	0.168	4.486	75.02	3.207
50	0.219	7.173	150.03	2.097
10	0.363	17.278	300.07	1.733

IV. Conclusion

Beta Alanine Thiourea Oxalate single crystals were grown succesfully using slow evaporation solution growth method. BATO crystallized in monoclinic structure and the unitcell parameters were found out from single cell X-ray diffraction analysis. Powder X-ray diffraction pattern revealed the good crystalline nature of the grown crystals. The functional groups present in the crystal were identified using FTIR spectral analysis. UV-Vis-NIR spectrum gave valuable information about the absorption of UV and visible light which involves the promotion of electrons in the π and π^* orbitals from the ground state to higher energy states. The crystal is highly transparent for a wide range which is attributed as an intensive property for device fabrication. The optical bandgap ,refractive index,extinction co-efficient,optical conductivity and electrical susceptibity were calculated using optical data. Large transmission in the entire visible region and shor t cut off wavelength enable the crystal to be a potential material for second harmonic generation. Nonlinear optical measurements were done with Kurtz Perry powder technique and BATO has SHG conversion efficiency 0.593 times that of KDP. From microhardness studies, it was found out that the crystal belongs to the category of soft materials. Mayer's index , yield strength , elastic stiffness constant , fracture toughness and brittleness index were calculated.From these parameters,the tightness of bonding between neighbouring ions and the mechanical strength to resist any deformation could be inferred.

Acknowledgement

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References

[1]. J.C.Brice.,(1986)Crystal growth processes,(ISBN 0470202688),Blackie(Glasgow and New York),298.
[2]. D.S.Chemla, J,Zyss,(1987) ,Nonlinear optical properties of organic molecules and crystals, Academic press,1:2
[3]. R.T.Bailey, F.R.Cruickshank,D.Pugh,J.N.Sherwood ,(1991), growth perfection and properties of organic nonlinear molecules ,Acta Crystallographica,A ,47:145-155
[4]. J.Thomas Jeyaprakash,L.Ruby Nirmala(2011), Synthesis spectral and thermal properties of bisthiourea zinc acetate single crystals, International journal of computer applications, Vol.6,0975-8887..
[5]. M.Subanandhini ,R.V.Krishnakumar ,M.Sivakumar,S.Natarajan ,9(2002),Crystal structure of beta alanine complex materials ,Acta Crystallographica E 58-307
[6]. S.Lincy Mary Ponmani, P.Selvarajan, N.Balasundari, D.Jencylin (2012), growth and characterization of β-alanine oxalate ,Journal of minerals and material. Charact. eng., vol.11,pp1069-1074.
[7]. P.S.Kalsi , Spectroscopy of organic compounds , fifth edition New age international(P)Ltd , New Delhi, 2002.
[8]. Briyan C Smith, IR Spectral interpretation, A systematic approach-CRC Press (1999) ,New York
[9]. R.Robert,C.Justinraj,S,Krishnan,R.Uthrakumar,S.Dinakaran,S.Jeromedas(2010),Spectral,optical and mechanical studies on LHC single crystals, Physica B 405 ,3248-3252
[10]. V.Krishnakumar ,R.Nagalakshmi ,Crystal growth and vibrational spectroscopic studies on Bisthiourea zinc choride NLO crystal ,Spectrochimica Acta Part A 61 (3)(2005)499-507
[11]. V.Krishnakumar R.John Xavier ,FT Raman and FT-IR spectral studies of 3-mercapto -1,2,4 triazole ,Spectrochimica Acta Part A 60 (3) (2005) 709-714
[12]. S.Annie Roshan , Cyriac Joseph , M.A.Ittayachen Growth and characterization of a new metal organic crystal Potassium thiourea bromide, Material Letters,Vol. 49 (2001) 299-302

[13]. T. N.Tigau , V. Ciupina , G.Prodan , G.I.Rusu , C.Gheorghies , E.Vasile ,Influence of thermal annealing in air on the structural and optical properties of amorphous antimony trisulfide thinfilms, Journal of Optoelectronics and advanced materials Vol. 6 (2004) 211-214
[14]. A mit Kumar Chawla, Davinder Kaur, Ramesh Chandra, Structural and optical characterization of ZnO nanocrystalline films doposited by sputtering,Optical materials, Vol.29(2007) 995-998
[15]. J.Madhavan ,S.Aruna ,P.C.Thomas, M.Vimalan ,S.A.Rajasekar ,P.Sahayaraj , Growth, and characterization of L-Histidine hydro chloride monohydrate single crystals ,Crystal Research and Technology Vol. 42 (2007)59-64
[16]. A.G K unjomana , K.A.Chandrasekaran ,Microhardness studies of GaTe whiskers, Crystal research and technology., Vol.40 (2005)782-785
[17]. B.W.Mott , micro indentation hardness testing, Butterworths , London , 1956.
[18]. J.Bennet Charles , F.Gnanam , Vicker's micromechanical indentation of NaSbF7 and Na3Sb4 F15 single cryatals , J.Mater Science Letters , vol.9 165-166, 1990
[19]. R.Hanumantharao , S.Kalainathan ,Microhardness studies on NLO L-alanine single crystals , Bulletin of material science , Vol. 36, No.3(2013), 471-474.
[20]. K.Murugadoss, G.Pasupathi, Hardness studies on solution grown LPS single crystals , International Journal of Chemistry and Material Science ,(2015) ,3(1)