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PHYSIOCHEMICAL PROPERTIES OF AMMONIUM PENTA BORATE HEXAHYDRATESINGLE CRYSTAL: AN EFFICIENT MATERIAL FOR OPTICAL LIMITINGAPPLICATIONS

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Abstract

AmmoniumPentaBorateHexahydrate(AMPBH),aninorganicnonlinearoptical(NLO)material was grown by the process of slow evaporation technique (SET) in aqueous solution. Thesynthesized (AMPBH) was characterized by single crystal X- ray diffraction study to affirm the structure(monoclinic), lattice parameters and space group P21/n. The functional groups in the material has beenanalyzed by FT-IR and FT-RAMAN studies in the range 4000 and 500 cm^{-1}. The optical absorption wasdeterminedfromtherecordedUV-Visiblespectraandenergygapwasevaluatedandthevalueis5.56eV.Thestudyonhardnessinfersthecrystalassoft materialcategory.Thedielectricnaturewasexaminedand Jonscher'slawconfirmstheconductivitymechanism withs=0.984.Laserdamagethreshold study using an Nd;YAG laser (1064nm) having pulse width 10 ns was also carried out. Theluminescencenatureofcrystalswasinvestigatedintherange300-800nmandconfirmedgreenandvioletfluorescenceemissionspectra.Temperatureofdecompositionandthermalstabilitywereinvestigatedusing TG and DTA thermaltechniques.UsingGaussianbeamofHe-Nelaserofwavelength,theZ-scanmeasurementrevealsnegativenonlinearityi.e.,self-defocussing,saturationabsorptionbehaviour andthereby the thirdordernonlinearsusceptibility$\chi(3)$were alsoevaluated.

Keywords: Nonlinearopticalcrystal;Borate;Luminescence;Z-Scan;

1. Introduction

The synthesis of nonlinear optical materials to fulfill their contribution in the domain of lasertechnology, optical data storage, optical communication and high speed information technology isgreatlyneedful[1,2].

Frequency conversion materials have the stability to break the restriction in optical spectrum inordertobe utilized innonlinearopticalapplications. The desired requirements of theNLO materialsrely on large transparencyrange,highnonlinearsusceptibility,fastnonlinearresponse andhigherdegree of laser damage threshold (LDT)[3]. Now, as the surge of polyborate salts occupying a vastposition in developed applications involving fluorescence, piezoelectric, nonlinear optical (NLO) andporousmaterials [4-5],theversatilityof boratesisgreatlyattractive.

Inorganic borate based crystals are found to possess high transparency in the UV regionand speciality of exhibiting different structures [3] emanating from special bonding properties of boronatom which coordinate with three or four oxygen atoms resulting [BO_3] or [BO_4] groups (AMPBH).Many authors reported borate based materials; Photoinduced NLO effects in doped δ-BiB_3O_6 crystals byMajchrowski et al [6]. Structure-property relationships of inorganic NLO crystal by Chang et al [7] inearlier studies in literature paved way to new series of borate based crystals [8-10]. Also Cook and Jaffeanalysedthepiezoelectricandelectricpropertiesof Ammoniumpentaborate(AB5)[11].C.Chenexplained that the anionic group $[B_5O_6 (OH_4)]^-$ or $[B_5O_8 (OH_2)]^{3-}$ is responsible for NLO susceptibility ofAB5[12].Alsotheadmiringphysicalpropertiespossessedbyboratesnamelypiezoelectricity,birefringencean despeciallynonlinearopticalnaturearesignificantlyacknowledgedowingtomultifunctionofborateattributedto boro-oxygen(anionicgroups)configurations.Researchersaremeeting a great challenge in design of materials governing the borates in tuning the assembling of theanionic groups. Borates which hold on of both water molecules in it which has poly anions in its crystalstructure.

Borate based NLO materials namely Potassium Borate, Potassium Pent borate (KPB), SodiumTetra borate, Strontium Tetra borate (SrB_4o_7), Lanthanum Calcium borate ($La_2CaB_{10}O_{19}$), and Bariumstrontiumboratehasbeenextensivelystudied[13]showingstability,higherlaserdamagethreshold

with enhance optical feature and transparent nature in UV region, provides greater difference in theelectro negativity ofB and O atoms which provide the basiccharacteristics ofborates [14]. A fewboratebasedcandidatewasalsoinvestigatedforfourthandfifthharmonicgenerationusingNeodymium-YAGlaser.

Moreover, Boron and its compounds have a broad range of applications in industry. Especially,boric acid is a well-known medium and its potential rich chemistry has recently been discovered. InBorate materials, the boron atom typically joined with three or four oxygen atoms form $[BO_3]$ or $[BO_4]$unitsandtheseunitssharecommoncornersprovidingvariousbuildingblockswithdifferentboronatomsforming clusterinasupramolecularmagnesoborate[15].MeantimeB_2O_6unitwithBO_4tetrahedral cluster was synthesized under high pressure with more flexibility was also reported and haveled to the diversity of more borate structures where as far as now more than 2000 borates were reported[15].

Borate crystals of Potassium and Ammonium are excellent non-linear optical materials which isuseful in laser techniques [16] also showing lower absorption to develop Ultraviolet NLO materials.Ammonium pentaborate is a suitable solvent for metal oxides, it is utilized in the process of welding,soldering, and brazing fluxes for stainless steel or nonferrous metals [17]. The effect of shock waves toenhance the optical characteristics of Ammonium Pentaborate Hexahydrate material was studied byAnandarajandJothi[18].

InthepresentworkweharvestedAmmoniumpentaboratehexahydrate,analkalineboratecrystals from the reaction of Ammonium carbonate, water, and boric acid. Present study includes thesynthesis and growth, single crystal diffraction study, optical characterization, FTIR and FT-Raman,Laser damage threshold study, dielectric, hardness and for the first time Fluorescence andthird ordernonlinearcharacterizationofAMPBHisreported,asuitablecandidatefornonlinearopticalapplications.

2. Experimental

2.1 Materialsynthesisandcrystalgrowth ofAMPBH.

AmmoniumPentaBorateHexaHydratewassynthesizedfromthestartingmaterialsAmmoniumcarbonateandboricacidofanalyticalgrade(AR)procuredfromMerckChemicals.The

calculated amount of Ammonium carbonate and boric acid were mixed in stoichiometric molar (1:2)ratio in deionized water at normal temperature. After continuous stirring for 9 hours, the homogenoussolution was filtered followed by slow evaporation of the solvent to obtain the material. After 20 daysoptically colorless and good transparent crystals were harvested formed after spontaneous nucleationprocess.The photograph ofas grown crystals ofvarying sizes are depictedin Fig.1(a,b).

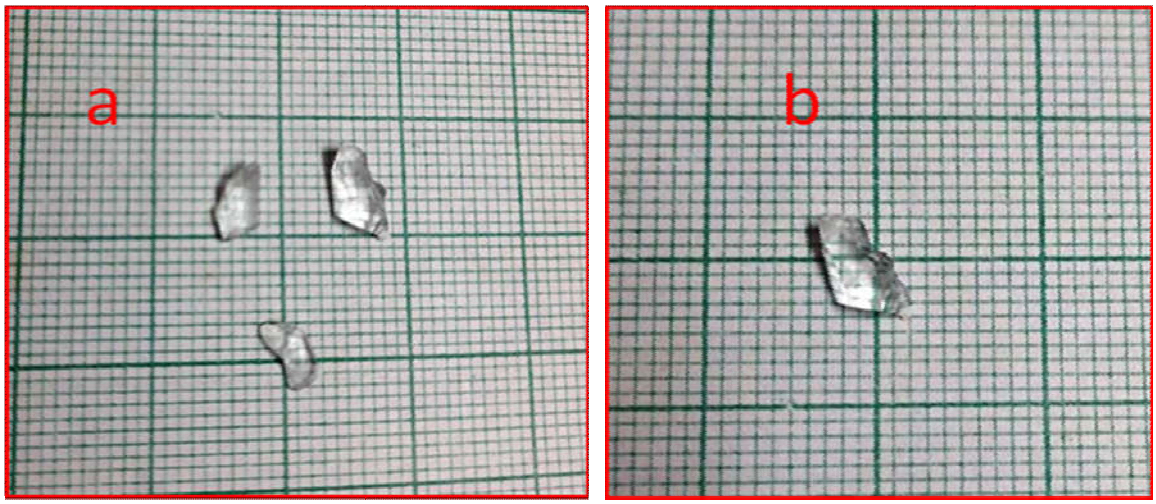

Fig. 1.(a)&(b) As growncrystal of AMPBH

3. Resultsand discussion

3.1 Singlecrystalx-raydiffraction

The grown crystal was given for single crystal X – ray diffraction to analyze the latticeparametersusingBRUKERKAPPAAPEXIICCDsinglecrystaldiffractometeraccompanyingMoKα(λ=0.71073Å).X-raydiffractionstudiesshowthatthecrystalcorrespondstothecentrosymmetric space group of P21/n holding monoclinic system and the cell parameter values aredepicted in Table 1 in accordance with reported work [18] whose structure holds a collection of fiveBoron with ten Oxyanions and six water molecules.The structure and crystal diffraction pattern ofAMPBHis representedinFigure.2.

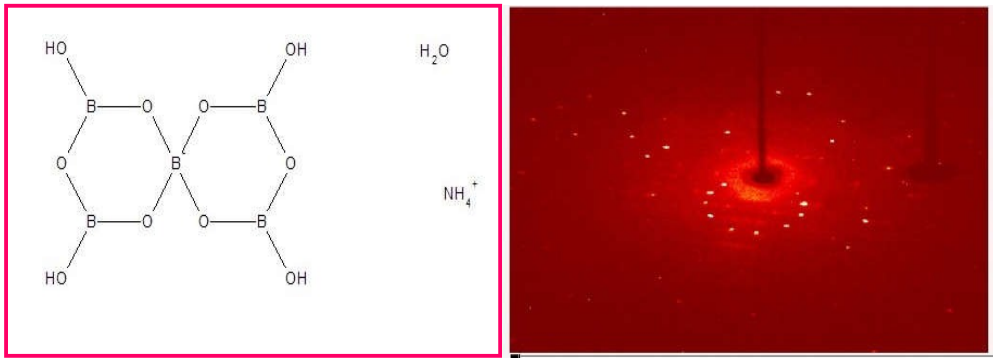

Fig. 2.Structure and Crystal diffractogram of

AMPBHTable1.LatticeparametersofAMPBHsinglecrystal

Cell parameters	Presentwork
Spacegroup	$P2_1/n$
a(Å)	7.18
b (Å)	11.34
c(Å)	7.18
α(°)	90
β(°)	100.16
γ(°)	90
Volume $(Å)^3$	574
CrystalSystem	MonoclinicP

3.2 FTIRandFT-RamanSpectral Analysis

FTIRinvestigationonAmmoniumPentaBorateHexaHydratewasdeterminedfromPerkinElmerSpectrophotometerintherange4000-500cm^{-1}wavenumberandisdepictedinFigure3(a)andFT-RamanspectralanalysiswasperformedusingBrukerRFS27FT-RamanSpectrometerportrayedinFig.3(b)respectively,wherethebondingofmoleculeinthecrystalelucidatedits absorptionnature.Thepeakoccurredin3125-3378cm^{-1}inIRisdue toNH_4stretchingandOHasymmetricstretching.TheN-Hstretchingvibrationpeaksobservedat3555cm^{-1}(IR)andat3551cm^{-1}(FT-

RAMAN) respectively. The O-H (hydroxyl group) stretching of vibrations of water is seen at 3378 cm^{-1} in IR and the corresponding peak at 3344 cm^{-1} in Raman spectrum. Also the stretching and bendingmodes of –OH groups are observed at 2459 cm^{-1} in IR and at 2460 and 2559 cm^{-1} in FT-Ramanspectrumcounterpart.

Thebandnoticedat1653cm^{-1}inIRisduetoNH4asymmetricbendingvibrationsandthecorrespondingpeakobservedat1602cm^{-1}inFT-Raman.Thepeakat1399cm^{-1}inIRcanbeattributedto the asymmetric stretching of the BO_3 groups and the counterpart observed at 1396 cm^{-1} in FT-Raman.Theborate crystals exhibitmolecular vibrationsin thethree IRspectralregions[19].

(i) in-between1500and1200cm^{-1}pertainingtoB-OstretchingoftrigonalB-OinBO3.

(ii) The B-O bending vibrations of borate crystal have the absorption bands in the frequency region782-1400cm^{-1}.

(iii) Bendingvibrations ofborateappearin-between 800and 650cm^{-1}.

Theabsorptionbandsobservedat1354,1248,1195,1102,1025,694and592cm^{-1}inIRandpeaksobservedinFT-Ramanspectrumcounterpartat1352,1240,1130,1003,865,710and616cm^{-1}respectivelycorrespondstoasymmetricandsymmetricstretchingB-Ovibrationsaredetailed inTable 2.

Table2.AssignmentsforFTIRandFT-RAMAN

FT-IR(cm^{-1})	FT-Raman(cm^{-1})	Assignments
3378	3382	O-HAsymmetricstretching
2459	2460,2559	Stretchingandbending modesof –OHgroups
1653	1602	NH_4Asymmetricbendingvibrations
1399	1396	AsymmetricstretchingofB-O
1354		B-OAsymmetricstretching
1195,	1205	B-O-Hbendingmode
1248	1240	CH_2Torsion
1102	1130	InplanebendingB-O-H
1025	1003	B-OTerminalasymmetricstretching
922	865	B-ORingstretching

782		B-ORingstretching
694	710	O-B-ORing symmetricbending
484		O-B-ORing bending
507		O-B-ORing bending
592	562	B-Onetworkin pentaborategroup
592	616	O-B-OTerminal bending

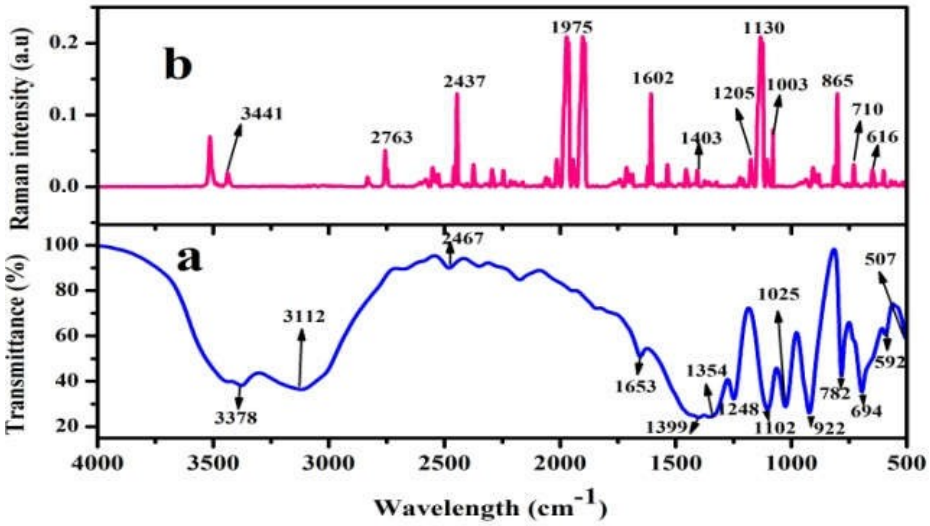

Fig.3.(a) FTIR(b) FT-Ramanprofileof AMPBH

3.3. UV-VisibleStudies

ByemployingPerken-ElmerLambda35UV-Visspectrometeroperatedintherange200-700nm, the transmittance nature of the crystal was analyzed which stands as a key requirement in the field ofphotonics and optoelectronics[19]. The UV-Visible spectra depicted in Fig.4(a) evinces that AMPBHcrystal possess low absorbance and high transmittance in the complete visible area having lower cut-offwavelengthat252 nm is the enticingfactorfor the materialspossessing NLOproperties.

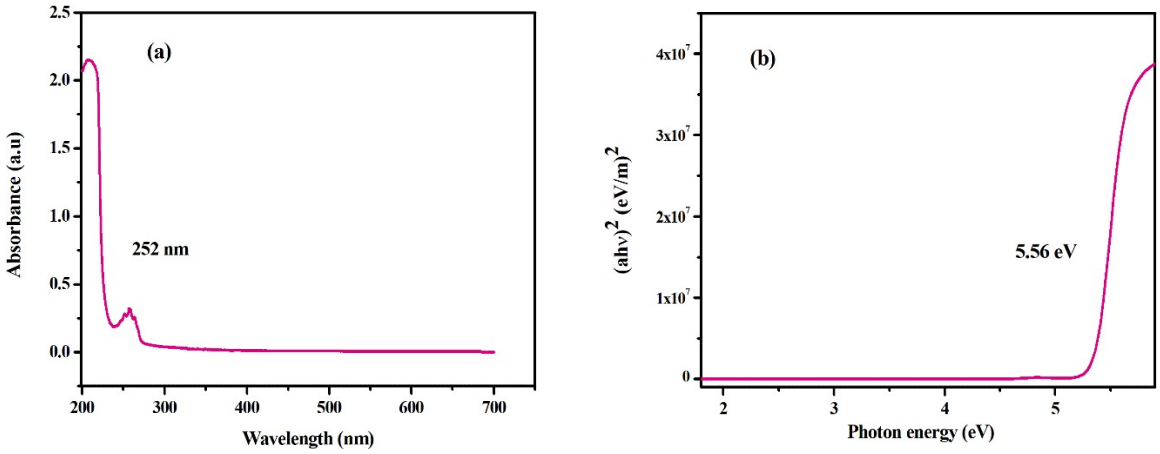

Fig.4.(a,b)UV-visiblespectrum, Tauc'splotforAMPBH

3.3.1 AbsorptionedgeandEnergygapdetermination

Thecalculatedabsorptionvalues(A)wasutilizedtoevaluatetheabsorptioncoefficient(α)utilisingthe followingequation:

$$\alpha = \frac{2.3026\log(1/T)}{t} \quad [1]$$

Where T, timplies the transmittance, tdefines thickness of the crystal. The absorption coefficient (α)was evaluatedby,

$$h\upsilon\alpha = A(h\upsilon - E_g)^{1/2} \quad [2]$$

Here A is a constant, E_g - energy gap, h infers Plank's constant, υ the frequency of the incidentphoton. The energy gap of AMPBH crystal was calculated from linear part of the tauc's graph plottedbetween $(h\upsilon\alpha)^2$ and hυ as depicted in Figure 4(b). The graph exhibits the realization of direct endorsedtransition for the titled material in the range 5.0-5.6 eV.From extrapolating the straight line down to$(\alpha h\upsilon)^2 = 0$, direct electronic band gap energy $E_g = 5.56$eV was found. Hence, AMPBH has broad opticalenergygapcan be anaptcandidatefor UVtunablelaser and NLOapplications.

3.3.2. UrbachEnergy

Theabsorption coefficient (α) asgiven bythe Urbachequation[20].

$$\alpha(h\upsilon)=\alpha_o \exp(h\upsilon/E_u) \quad [3]$$

denote $\alpha_o$as a constant, $E_u$pertains urbach energy, h signifies Planck's constant and υ indicates thefrequency of radiation. The plot of photon energy hυ and ln(α) is shownin the profile (Figure(4c)). ThecrystallinefeatureofAMPBHisfoundoutfromtheincreaseinvalueofαwithphotonenergyhυ,depicts high crystallinity in the grown crystal. The slope 3.3316 of the linear part of the graph wascalculated from log of the absorption coefficient (α) with photon energy (hυ) that explains that AMPBHhas highcrystallinenature[19].

The Urbach energy as evaluated from the reciprocal of the slope is 0.3002 eV. Moreover the low(0.3002eV) estimatedUrbach energysignifies minimumdefect inthe titleammomiumboratecrystal.

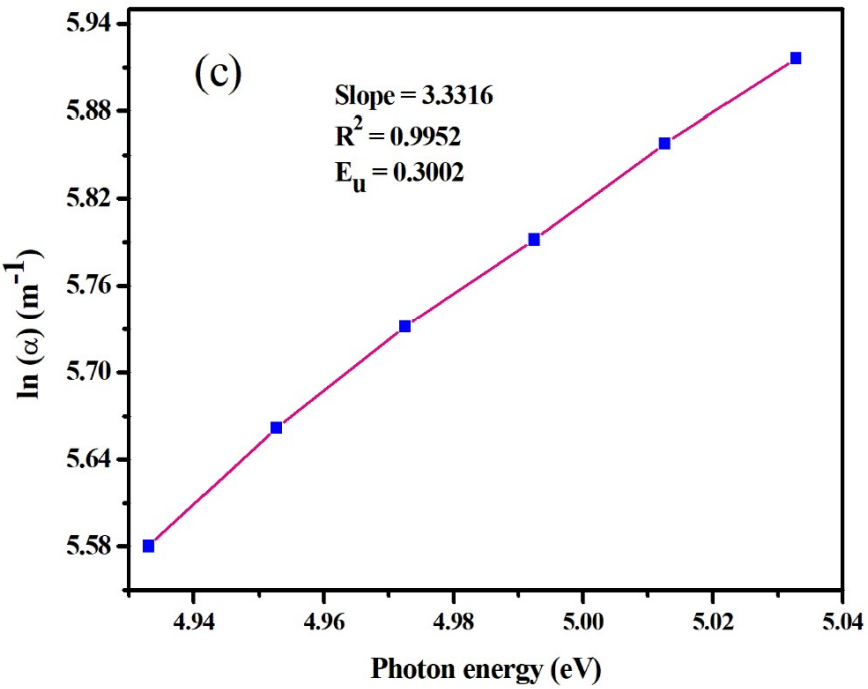

Fig.4c.Plot ofln(α)withphotonenergyforAMPBH

3.3.2 Opticalconstantdetermination

Usingthespectraofabsorption(Fig.4a),thedemandingopticalparametersnamelytransmittance, absorbance, reflectance, absorption coefficient and energy gap were valuated are essentialwhen dealing in the field of processing, tuning, calibrating and design of technology based devices.Inclusive determination of opticalconstants is needed as they promote bringing the conceptregardingtheopticalfeatureofthegrownmaterial.Thustheinfluenceofextinctioncoefficient(K)andreflectance(R) of crystal has been studied using the computed transmittance data. The inner efficiency ofthe appliance too confide on the domains such asabsorption coefficient and extinction coefficient (K)showingpartiallossoflightperunitdistanceinacollectivemedium.Theextinctioncoefficientis evaluatedusingtheformula:

$$K=\frac{\lambda\alpha}{4\pi} \quad [4]$$

Thegraphbetweenextinctioncoefficientandtwainreflectancewithphotonenergypredictsthatreduction of extinction coefficient with energy [19] as shown in Fig. 5(a,b). The reflectance (R) in termsof opticalabsorptioncoefficient shown belowas

$$R=1\pm\frac{\sqrt{1-\exp(-\alpha t)+\exp(\alpha t)}}{1+\exp(-\alpha t)} \quad [5]$$

Fig. 6(a,b) depicts the twain reflectance and extinction coefficient confide on absorption coefficient. It isunderstood that as the values of R and K change with photon energy and also depend on absorptioncoefficient α, the alteration of optical constants notably the α and E_g contribute significantly towards thefabricationof opticaldevices [21].

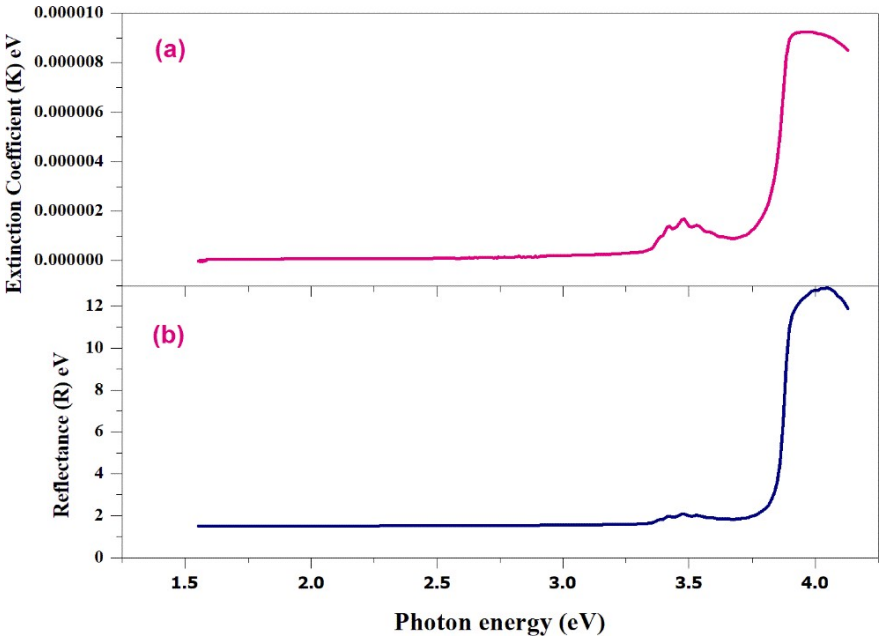

Fig.5(a,,b)Extinctioncoefficientandtwainreflectance(R)dependenceonphotonenergy(hυ)

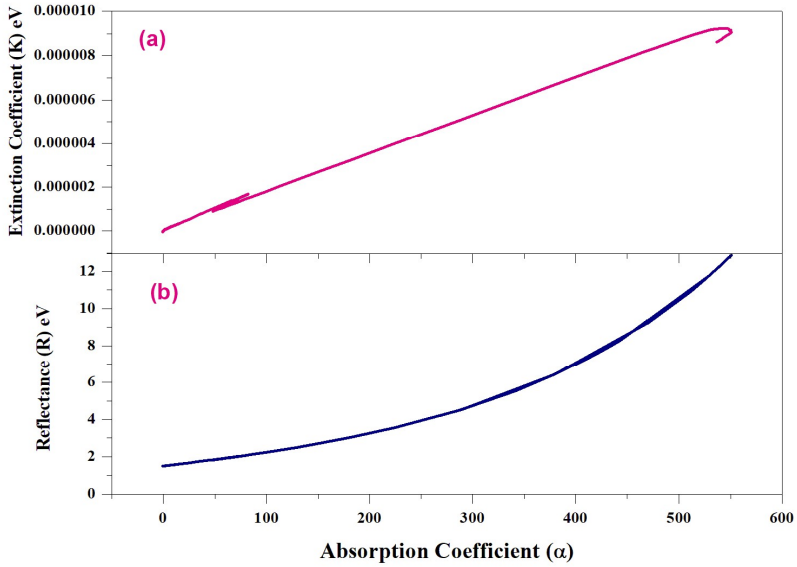

Fig.6(a,b)Extinctioncoefficientandtwainreflectance(R)dependenceonabsorptioncoefficient(α)

3.4. ThermoGravimetricandDifferentialThermalAnalysis(TG/DTA)

Thermogravimetricanalysis(TGA)andDifferentialThermalanalysis(DTA)standsasaprincipaltechniquestocharacterizethethermalstabilityofthegrownmaterial.ForAMBPHthetemperature withstanding point was explored by SII NANO TECHNOLOGY (MODEL TG/DTA 6200)operated between the temperature 20-800 C at a heating rate of 20 C min^{-1} under nitrogen atmosphere.Initially 2.032 mg was taken for the investigation. The TG/DTA portrayal of AMPBH is shown inFigure7.

Two main weight losses occur between 125 C-200 C causing liberation of water molecules and$NH_3$from AMPBH. The endothermic signal in DTA at around 200 C matches with TGA weight losscurve and also at around425C, the DTA and TGA shows a decline at this temperature(425C) wherethe second weight loss curve ends. Further heating, third weight loss appear at 425 C and continues till800 C with no further endothermic peaks in DTA and counterpart TGA displaying complete weight lossleadingto residueofthematerial finallyat800C,

Henceforththe AMPBHcrystal canbesuitablefor NLOapplicationsupto125C.

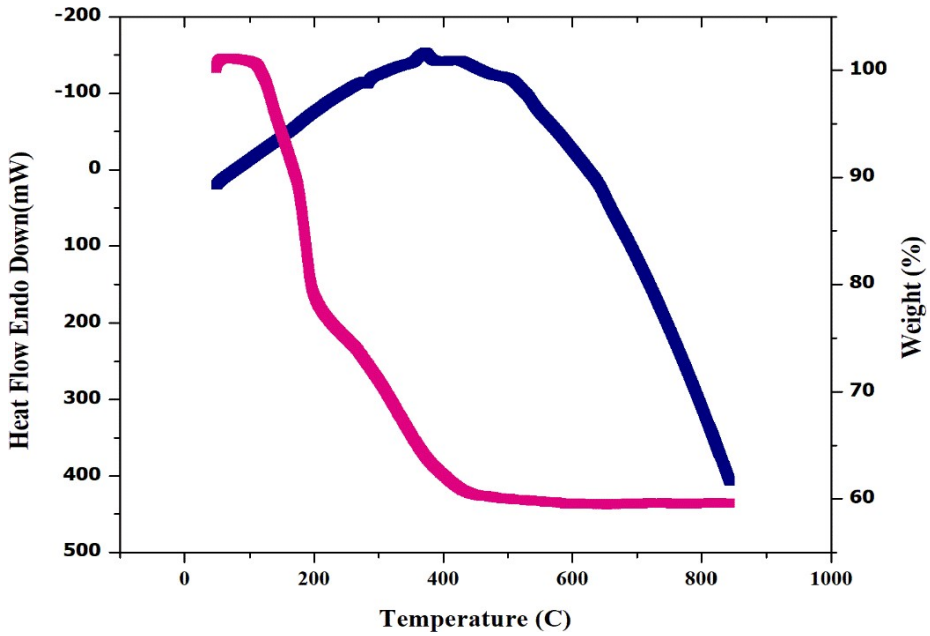

Fig.7.TG/DTAprofileofAMPBH

3.5. Dielectricstudies

Thedielectricconstant ofAMPBHwasestimatedusingtheexpression,

$$\varepsilon' = \frac{CdA}{\varepsilon_0} \qquad [6]$$

Here, d, C represents the thickness and capacitance of the crystal. The change in dielectric constant anddielectric loss with frequency for various temperatures are presented in Fig. 8(a,b) which depicts thatdielectric constant and loss decreases increases with frequency. For lesser frequency, dielectric constantgains larger value in view of the presence of all polarization mechanism since low dielectric constantmaterials has lesser measure of dipoles per unit volume when compared to the crystal possessing highdielectricconstant. Hencemeetsthecriteria in opto-electronicapplications.

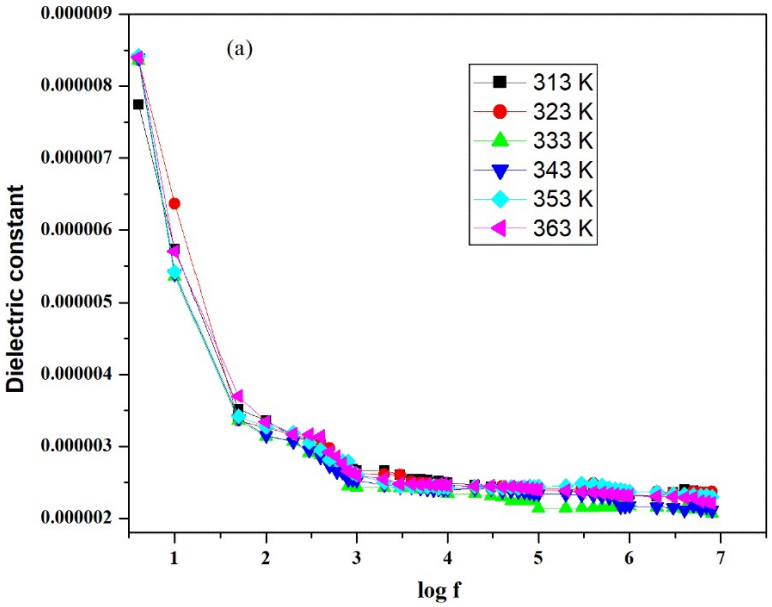

Fig.8.(a) PlotofLogf vsdielectricconstantofAMPBH

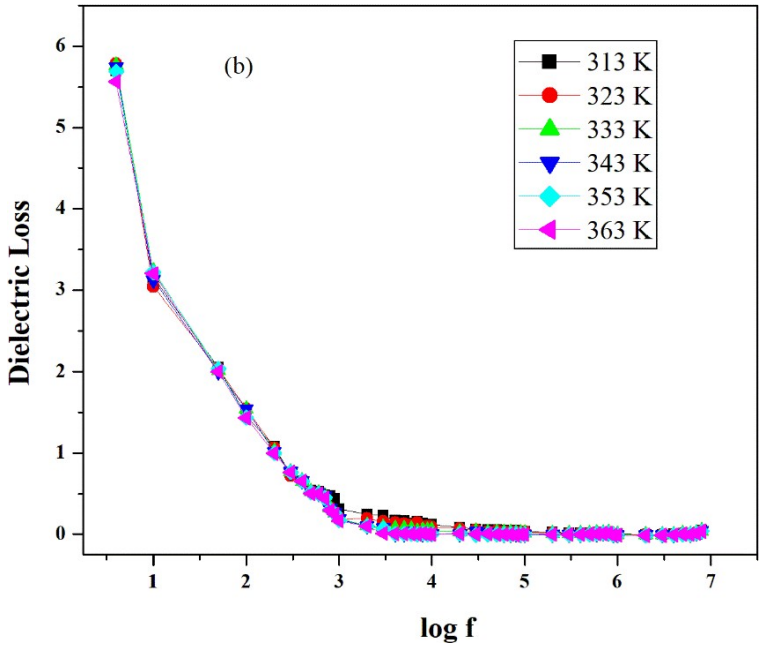

Fig.8.(b) Plotof Logfvsdielectric lossof AMPBH

3.5.1. ActivationEnergy

Activationenergyis obtainedfrom,

$$\sigma=\sigma_0 \exp\left(-\frac{E_a}{k^B T}\right) \quad [7]$$

Here,σ_{ac}– conductivity, T-temperature, E_a - activation energy, K_B - Boltzmann constant(1.38 x 10^{-23} J/K). The graph between log σ_{ac} and 1000/T is showed in Fig.9 from which the activationenergyis determined by theexpressionfrom the slope in thelinear portion,

E_a= -Slopex 1000x K_B [8]

The evaluated values of activation energy was found to be 0.0241, 0.0146, 0.0112 eV at 700 Hz, 3 KHz,20 KHz and at 3 MHz frequencies denotes that inferior values of activation energy, predicts less defectsin materials pertainingtotheirusefulnessin devicefabrications.

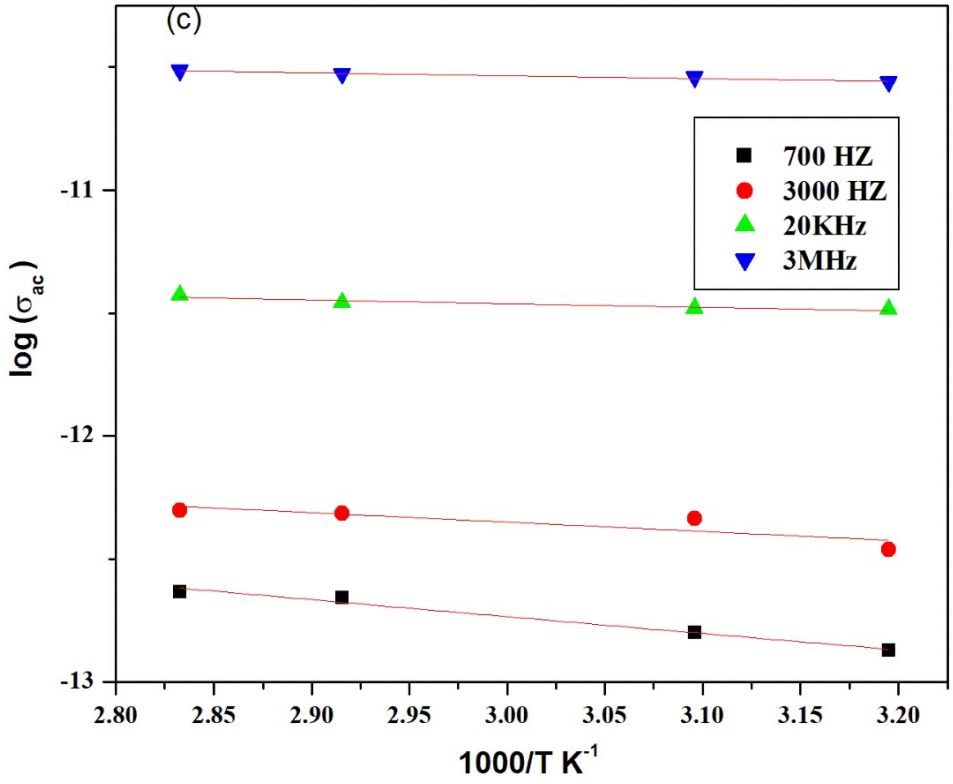

Fig.9.Plotof1000/T versesLog σ_{ac}

3.5.2. MechanismofConduction-Jonscher'spowerlaw

Therelationshipbetweenelectricalconductivityσ_{ac}andfrequencyseeninvarioussolidsconstituting polymers, glasses and crystalswas looked over by Jonscheris well acknowledgedby thepowerlaw [22],

$$\sigma_{a.c} = \sigma_{d.c} + A\omega^{S} \quad [9]$$

, where σ_{dc}infersDC conductivity that concludes the frequency (ω)independent plateau in lowerfrequency, A is a constant that depends on temperature rely on polarisation, and s - power law exponentthat lies in the middle0 < s < 1, that varywith materials. Figure 10 represent the specification ofJonscher's power law explored for the title material whose s = 0.984 established from the slope of thegraphleadstothegoodagreementofthepowerlaw.Theconductionprocedurerecognizedfromthe

graphinfersthatACconductivitystep-upalmostathigherfrequencyasaresultofhoppingmechanism [23]observedfromAMPBHcrystal.

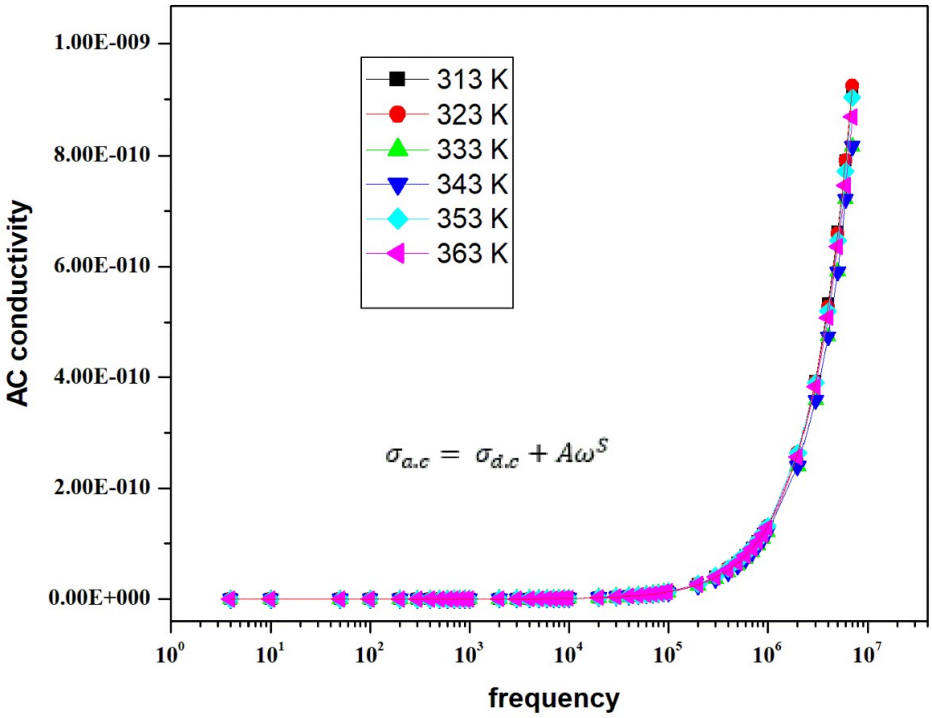

Fig.10. Plotof ACconductivityvs Frequency

3.6. Micro(mechanical) hardnessstudies

The microhardness study confirms the materials capacity in device fabrication by exploring themechanical strength. The strength of the materials depends on various parameters such as lattice energy,Debye temperature, heat of formation and interatomic spacing. The MH- 112 Vicker's microhardnessmeasurement on AMPBH crystal was done at room temperature and load of 25, 50, and 100 g wereapplied.

.TheVicker'shardnesswhichconnectstheappliedloadanddiagonaloftheindentwasevaluatedusingstandard formula

$H_v = 1.855\ (P/d^2)$ [10]

Where P implies applied load , dthe mean length of the indenter impression , and 1.8544 is a constant.Figure11(a)representsthedependenceofhardnessnumber(H_v)withappliedloadextendingfrom25-

100gforAMPBH,where$H_v$increaseswiththeincreaseintheloadisobservediswellconsideredasthereverseinde ntation sizeeffect[RISE] [24,25].

TheMeyer'sindexcoefficientwascalculatedfromMeyer'slaw[19],whichimpartsarelationbetweentheloadan dindentation diagonallength,

$$P=K^1 d^n \quad [11]$$

(or)

$$\log P = \log K_1 + n \log d \quad [12]$$

Where K_1 signifies constant and 'n' denotes Meyer's index. Work hardening coefficient 'n', ischecked from a plot drawn between log P vs log d as displayed in Figure 11(b). From the slope of thelinearstraightlinethevalueof'n'is3.70.ForthenormalRISEbehavior,theconditionisn<2.Whenn > 2, it infers reverse RISE behavior. This is good coincidence with the experimental data pointingtowards reverse RISE. As per the statement given by Onitsh [26], work hardening coefficient should bebetween 1 and 1.6 for harder materials and above 1.6 for softer category. Hence, AMPBH can be termedassoftmaterial category.

$$\sigma_y = \frac{H_v}{3}(0.1)^{n'-2} \quad [13]$$

Where n′=n+2.

AgraphbetweenthevariationsofloadPwithyieldstrength$\sigma_y$iscalculatedforAMPBHcrystal(Figure11(c)).

Theelasticstiffnessconstant (C_{11})isalsofigured out fromWooster'sempirical formula[27],

$$C_{11} = (H_v)^{7/4} \quad [14]$$

The elastic stiffness constant recognizes the nature of bonding between neighbouring atoms. A graph isbetween load P vs. stiffness constant C_{11}illustrated in Figure 11 (d) furnish that the stiffness constantincreases with increase of load. The greater the stiffness constant C_{11}lead to the conclusion that thebinding forces between theionsarequiteenergetic.

TheKnoop'shardnessnumber (H_K)isalsodeterminedfrom,

$H_K(Kg/mm^2)=14.229\frac{P}{d^2}$ [15]

From the tabulated values of load P and H_K (Knoop's hardness number), the graph is plotted (Fig.11e). The calculated mechanical parameters are tabulated (Table 3)

3.6.1 Heys-Kendall(HK)Approach

The point of view regarding the study of HK, which initiates the determination of load independent parameter hardness[28], from the relation

$P = W + A_1 d^n$, where W refers initiation of plastic (permanent) deformation (in grams). A_1 is the load-independent constant and the exponent n=3.70. The quantities W and A_1 were concluded from the graph load P vs. d^2 as shown in Figure.11f. The corrected load independent hardness H_{HK} value (Table4) of AMPBH was valuated from:

$H_{HK}= 1854.4A_1$ [16]

From the hardness analysis AMPBH crystal proves that has sufficient mechanical strength for various NLO device fabrications. The estimated mechanical parameters are listed in the Table 3.

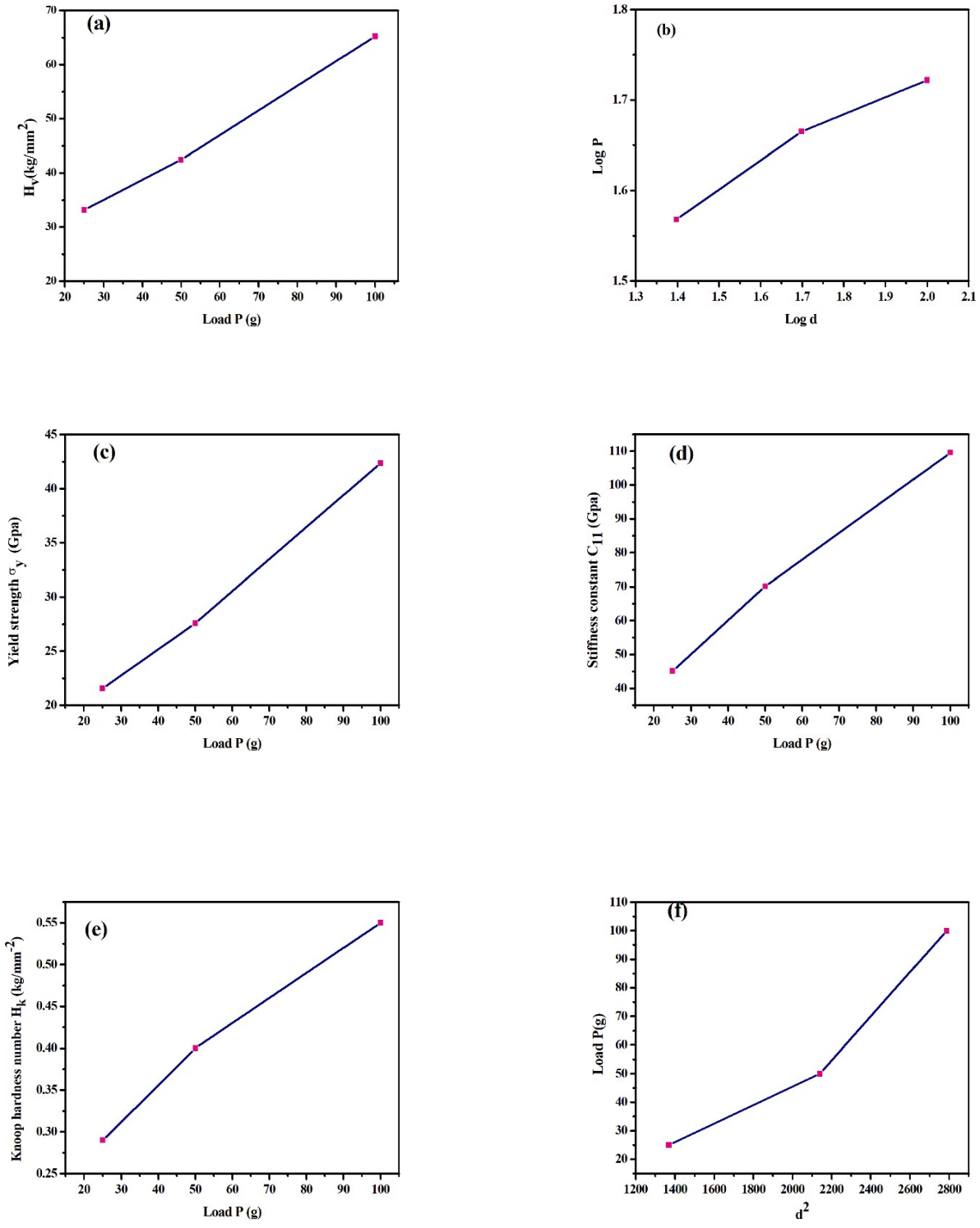

Fig.11(a,b,c,d,e)Microhardness , Meyers plot,Yield strength,Stiffness constant,Knoop's hardnessnumber,load Pvs. d^2

Table3:ComputedMechanicalparameters

load P(g)	n	H_v(kgmm^{-2})	σ_y(G Pa)	H_K(Kg/mm^2)	C_{11}(M Pa)
25	3.70	33.18	21.56	25.46	4.495
50	3.70	42.44	27.58	32.56	6.915
100	3.70	65.18	42.35	51.03	14.652

Table4: CalculatedHKconstantW, A_1, andH_{HK}

HKconstant	Results
ResistancePressure(W)	-44.0682(g)
Loadindependent constant(A_1)	0.0482(g/μm^2)
Correctedloadindependenthardness(H_{HK})	89.38208(g/μm^2)

3.7. PhotoluminescenceStudies(PL).

PLspectroscopyplaysavitalroleinexploringtheelectronicstructureandassessingthetransparencyofthesolidanddiscoveringtheenergystatesexistingbetweenvalencebandandconductionbandresponsibleforradiativerecombination[28].Thephotoluminescencespectrumobservedintherange300-800nmisdelineatedforAMPBHshowingroomtemperaturephosphorescencewithanexcitationwavelengthof253nmusingPERKINELMERLS45Spectrophotometer (Figure 12). The PL spetra portrays one green fluorescence peak at 506 nm (2.45eV) , one cyan(blue) emission peak at 463 nm (2.68 eV)and one violet fluorescence peak at 384nm(3.23 eV) which emerges as a result of disappearance of self-trapped excitons linkedwith the moleculartransitions within theBO^- group[19] makes AMPBH suitable in optical data storage devices[29].Theblue phosphorescence spectra emerges as a result of high energy photons and the generation of greenphosphorescence due to low energy photons [30].In ammonium boratecrystalsB-O provides the π-bond orbitals and or π^* anti-bond orbitals in phosphorescent excited statesthat paves way to synthesizeadvancedclass ofphosphorescentmaterials applicablein tunablelasers[30].

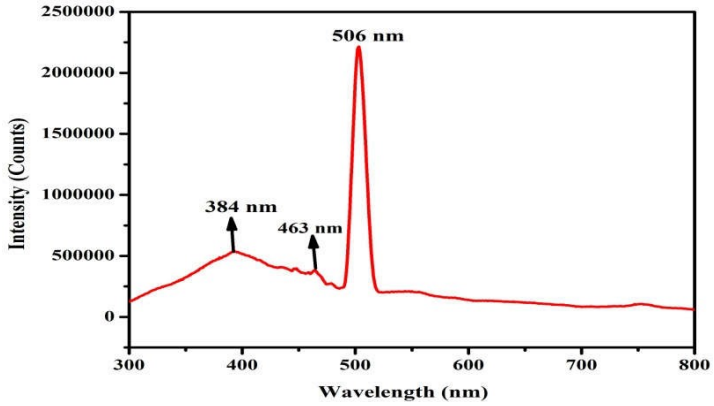

Fig.12.EmissionspectrumofAMPBH

3.8. LaserDamageThreshold(LDT)Study

LDTisusuallyconnected toriseintemperaturein thematerials leadingto strain-inducedfracture evolved by electron avalanche, multi-photon absorption and ionization processes [31]. LDTmeasurement was performed by Q-switched Nd:YAG laser source with primitive wavelength (1064 nm,6ns,10Hz).MultipleshotLDTequivalentoftitlecrystalwasevaluatedfrompowerdensityexpression:

$$\text{Powerdensity}(P_d) = E/\tau\pi r^2 (GW/cm^2) \quad [17]$$

[WhereE,τ,rrepresentsinputenergy(mJ),pulsewidth(ns),radiusofthelaserbeamspot(mm)]is $10.59 GW/cm^2$, establishedthematerialssuitability forhigh powerlaserapplications.

3.9. Z-Scanmeasurements

Highly sensitive and a standard method for determining nonlinear optical properties of materialssuch as solids, liquid solutions and thin films like absolute magnitude and sign of nonlinear refractiveindex(n_2),nonlinearabsorption(NLA)andnonlinearrefraction(NLR)wasdevelopedforwideapplications in the field of optical imaging, multi-photon polymerization including optical switching isthemethodofZ-scanintroducedbySheik-Bahaeetal[32].Heretheclosed(Fig.13a)andopenaperture(Fig.13b)configurationsarediscussedconnectedtothemeasurablequantitiesnonlinearabsorption (NLA) and nonlinear refraction (NLR) associated with the imaginary and real part of the thirdorder nonlinear susceptibility $\chi(3)$, provides information about the properties of the material. In the Z-scantechniqueusedtocharacterizetheAMPBH,He-Nelaserbeam(Gaussianbeam)ofintensity5mW(λ=632.8nm)wasemployedasasource,withbeamdiameter0.5 mmandaconvexlensoffocal length

30 mm through which a Gaussian beam was passed. In this procedure, the Z-scan depends in thedistortions generated in the spatial and temporal profile of input beam passing through the sample. Totaltransmitted intensity with respect to the radiations at the sample which is being translated is all due tomulti-photonabsorptionmaybelimitedtotwo-photonabsorption.Thevariationinfarfieldtransmittance beam intensitywas measured through theclosedapertureusing adigital power meter(Field Master GS-coherent). The spatial variation of refractive index caused due to the temperaturedistribution on surface of the crystal leads to phase distortion in incident beam enables to evaluate thephase-shift($|\Delta\varphi|$) in transmitted beambythe relation,

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}\Delta\Phi_0 \quad [18]$$

Where(ΔT_{P-V})denotesvariancebetweenpeakandvalleytransmissioninclosedapertureassessmentand Sisthelinear transmittance aperture and is approximated by,

$$S = 1-\exp\left(\frac{-2r_a^2}{\omega_a^2}\right). \quad [19]$$

$r_a$is the radiusofthe apertureand $\omega_a$isthe beamradiusandspotdiameterat theaperturesubsequently.Thenonlinearrefractiveindex (n_2) can beestimatedby usingthe relation:

$$n_2 = \frac{\Delta\Phi_0}{KI_0L_{eff}} \quad [20]$$

Here $|\varphi|$ represents on axis phase shift, where I_0 is the on-axis irradiance at focus (Z=0) (I_0 , the intensityof the laser beam at focus (Z=0) and L_{eff} istheoperativethickness of the sample canbe determinedby

$$L_{eff} = [1-\exp(-\alpha L)]/\alpha \quad [21]$$

Ldenotesthesamplelength,αrepresentsthelinearabsorptioncoefficient,andkrepresentsthewavenumber(k = 2π/λ).

Inopenaperture(Fig.13b),thenonlineartransmissionofsamplewithoutaperturewastallied. Thisadmitsustoresolvethe nonlinearabsorptioncoefficient βfrom openaperture signature,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad [22]$$

Wherefore$\Delta T=1-T_v$,whichthat$T_v$specifiesvalleytransmissionvalueinopenaperturedetermination.This parameter discloses negative value for saturation absorption and positive for twophoton absorptionandhencehas anadvantagetobe utilized for opticalpowerlimiting processandsignalprocessing devices[28,33].

Thereal andimaginary parts ofthe thirdorder nonlinear opticalsusceptibility (χ^3)were establishedusing theformula:

$$\mathrm{Re}\chi^{(3)}(esu) = \frac{10^{-4}(\varepsilon c^2 n^2 n_2)(cm^2)}{\pi}\left|\frac{}{(W)}\right| \quad [23]$$

$$\mathrm{Im}\chi^{(3)}(esu) = \frac{10^{-2}(\varepsilon c^2 n \lambda \beta_0)(cm^2)}{4\pi^2}\left|\frac{}{W}\right| \quad [24]$$

Where,ε_0 isthevacuumpermittivity($8.8518\times10^{-12}Fm^{-1}$)and$\lambda$isthewavelengthoflaser.Thethirdorder nonlinear opticalsusceptibility(χ^3)ofthe crystalisfiguredoutfrom the relation:

$$\left|\chi^{(3)}\right| = \sqrt{(\mathrm{Re}(\chi^{(3)}))^2+(\mathrm{Im}(\chi^{(3)}))^2} \quad [25]$$

Thethirdordernonlinearparametersvaluescheckedfromdata'sandformulasweretabulatedinTable5for AMPBH.

In normalized transmittance curvature collected from the closed aperture (Fig.13a) Z scan data,we can able to look that peak is followed by valley suggesting that the sign of refraction nonlinearity isnegative i.e., self-defocussing. The self-defocussing effect turns out as a result of alteration in refractiveindex dependence on temperature and hence this property is enforced in the shielding of optical sensornamely night vision devices where IR night-vision couples with IR illumination having spectral range700-1000nm[29,22].

The nonlinear absorption coefficient (β) value is 0.0209 x $10^{-4}cm^2W^{-1}$ and its positive valuestipulates that two photon absorption have occured [28].The nonlinear optical properties of AMPBHmake it as a capable possible material in the field of optical limiting application.The ratio of closed toopen normaltransmittancefunctionisportrayedintheFig. 13(c)and Fig. 13(d).

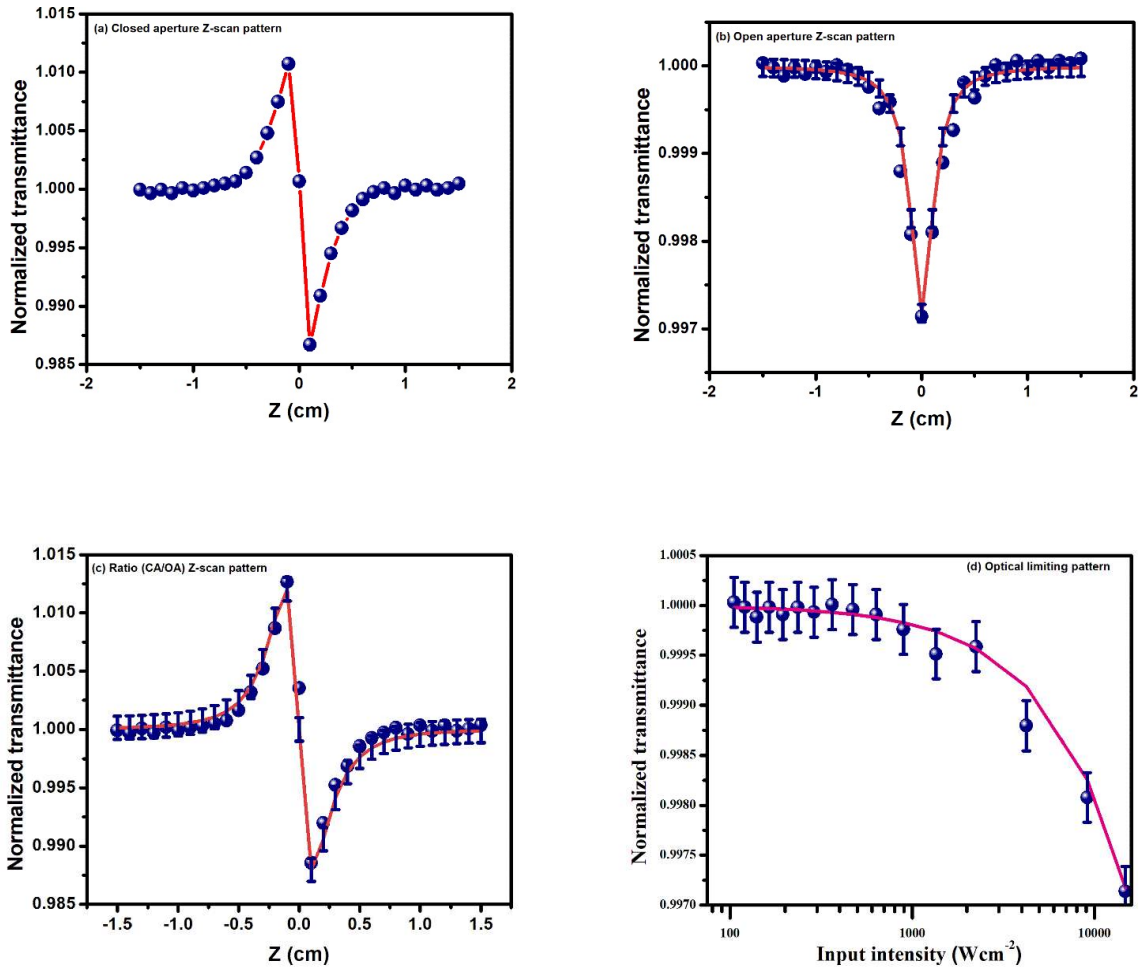

Fig.13.(a,b,c,d) Closed apertureprofile,Openapertureprofile,Ratioofclosedtoopen z-scantraces, Normalizedtransmittance versusInputIntensity of AMPBH

Table5:ObtainednonlinearopticalparametersfromZ-scanmeasurementsofAMPBH

Third-ordernonlinearproperties	Measured values
Nonlinear refractive index	$3.726\times 10^{-10}cm^2W^{-1}$
(n_2)Nonlinear absorption coefficient	$0.0209x10^{-4}cm^2W^{-1}$
(β)Real susceptibility(χ^3)	1.739×10^{-8}esu
Imaginary susceptibility	4.129×10^{-8}esu
(χ^3)Absolutesusceptibility(χ^3)	4.480×10^{-8}esu

4.Conclusion

The alkaline borate symmetric AMPBH crystals were grown and harvested in three weeks byslow evaporation method. The lattice parameters of AMPBH was known from single crystal x-raydiffraction study and found to possess monoclinic system with centrosymmetric space group. FTIR andFT-Raman spectral study established the functional groups comprising the crystal. The evaluated opticalparameters from UV-Vis spectral data clearly suggest the alkaline borate material could be utilized inoptoelectronics and fabrication of devices. AMPBH is thermally stable up to 125 ˚C which was revealedfrom TG/DTA analyses. The low dielectric constant and dielectric loss of AMPBH in the high frequencyregion shows good optical quality. PL spectral profile exhibit sharp green fluorescent peaks at 506 nm,463 nm and at 384 nm corresponding to green and violet fluorescence spectra. The microhardnessVickerstestconcludesthatthetitlealkalineboratecrystalfallsundersoftmaterialcategory.Theno nlinear refractive index (n_2), absorption coefficient (β) and third-order nonlinear susceptibility χ^3,(4.480×10^{-8} esu) calculated from Z-scan along with optical and spectral analyses concludes that thealkaline borate crystal AMPBH could serve as an admirable candidate for opto-electronic, photonic andnonlinear opticalapplications.

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