OPTICAL, THERMAL, LASER DAMAGE THRESHOLD, DIELECTRIC STUDIES AND Z-SCAN TECHNIQUE OF NOVEL SEMIORGANIC NLO MATERIAL: SODIUM BORO SUCCINATE (NaBS)

A. VIJAYALAKSHMI[1], VIDYAVATHY BALRAJ[2]

Single crystals of sodium boro succinate (NaBS) a new semiorganic non linear optical material were grown by slow evaporation technique. Crystals of NaBS was grown in a solvent of ethanol-water in the ratio of 1:1 through recrystallization. With X-Ray diffraction, the crystal structure and lattice parameters were determined. The compound crystallizes in the Monoclinic system with a = 7.7421(2) Å, b = 14.9136(3) Å, c = 12.6480 (3) Å and β = 96. 1644 (3) °. Some of the fundamental data of valance electron, plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal were calculated. The optical transmittance of the crystal was analyzed using UV-Visible. Thermal stability of the crystal analyzed by TGA/DSC studies. The potential of the crystal to laser light analyzed by Laser damage threshold studies. The dielectric constant and loss were studied as a function of frequency by dielectric studies. Z-Scan test performed to know non linear refractive index, nonlinear absorption coefficient and third-order nonlinear optical susceptibility.

Keywords: slow evaporation technique; UV studies; Laser damage threshold; Dielectric studies; Z-scan technique;

1. Introduction

Many novel design and synthesis of organic and inorganic NLO materials with high -linear susceptibilities is in the state of dynamic research [1][2]. Special consideration is given in producing functional alteration and inducing novel properties that are lacking in the parent crystal. Growth of non-linear optical materials is given high priority due to their possible application in Lasers and optical wave guide where there is a essential for secondary harmony generation (SHG) [3]. Nonlinear optical (NLO) materials are very much significant in the field of nonlinear optics because of their greater impact on Information Technology and other Industrial applications. Because of its various applications

[1] Department of Chemistry, RMK. Engineering College, Kavaraipettai, India. e-mail: harshiniraja16@gmail.com

[2] Department of Chemistry, Velammal Engineering College, Chennai, India, e-mail: vidyavathybalraj@gmail.com

in many fields, there has been a rising interest in crystal growth process to meet the demand. Single crystals can be used in various fields like infrared detectors, polarizers, solid state lasers, piezoelectric, acousto-optic, photosensitive materials, semiconductors and crystalline thin films for computer manufacturing industries and microelectronics. The process of synthesis of single crystals and its characteristics towards device manufacturing have been accepted great impulse due to their importance in both applied research and academic research.

The wide range of borate family is appropriate for chemical playground which adopted by many material researchers and scientists, due to the wide variability of the borate crystal chemistry which allows manufacturing of different structure types [4].Among all the borate structures studied till date about 36% are non-centrosymmetric and 15% are inorganic crystal structures [5]. Compared to other commonly used NLO materials such as lithium niobate (LN) and potassium di hydrogen phosphate (KDP), borate crystals are superior due to its high transmittance at wavelength down to 155 nm and also the high threshold value. The borate crystals have gained considerable popularity as NLO materials for its high transparency in the UV region and higher resistance against laser induced damage [4][6]. Many exquisite crystal materials of borate family were discovered CsB_3O_5 (CBO) [7], $CsLiB_6O_{10}$ (CLBO) [8][9], and $K_2Al_2B_2O_7$ (KABO) [10] and there are other several borate crystals that are available today which are significant in the field of optical industry . Similarly, succinic acid broadly used in many industrial applications like fabrication of high electron mobility transistors (HEMTs) [11]. The synthesis of NaBS scope includes, based on the excellent properties of semiorganic NLO materials such as potassium boro oxalate [12], Lithium bis L-malato borate [13], potassium bromalate [14] potassium boro succinate [15] and GdAl3(BO3)4 [16]

Sodium boro-succinate crystals was successfully synthesized through slow evaporation and have been characterized by single crystal, UV-Vis spectroscopy, thermo gravimetric analysis (TGA), differential scanning calorimetric analysis (DSC), dielectric studies and Z-scan test.

2. Experimental procedure

2.1 Synthesis and crystal growth:
Aqueous solution of sodium boro succinate (NaBS) was synthesized from sodium carbonate (Sigma Aldrich), boric acid (Sigma Aldrich) and succinic acid (Sigma Aldrich) in the ratio 0.5:1:2. The calculated amount of boric acid and succinic acid were thoroughly dissolved in double distilled water. Under continuous stirring, required amount of sodium carbonate was slowly added and stirred well for about 6 hours in a magnetic stirrer till dryness. The synthesized salt was dissolved in ethanol-water (1:1) solvent, and left undisturbed for slow

evaporation. After 20 days of solvent evaporation, supersaturated crystals of NaBS with dimension of 18 X 12 X 2 mm^3 was obtained. The grown crystals of NaBS are shown in Fig. 1.

Fig.1.Crystal image of NaBS

3. Results and discussion:

3.1. Single crystal X-ray diffraction and basic parameters from XRD data

Single crystal X-ray data collection was performed by Bruker Kappa diffractometer with Mo Kα radiation using ω/2θ scan mode. The XRD study reveals that the crystal belongs to monoclinic system with the space group P21/n. The lattice parameters a= 7.7421(2) , b = 14.9136(3) and c = 12.6480(3), and v=1451.93(6).
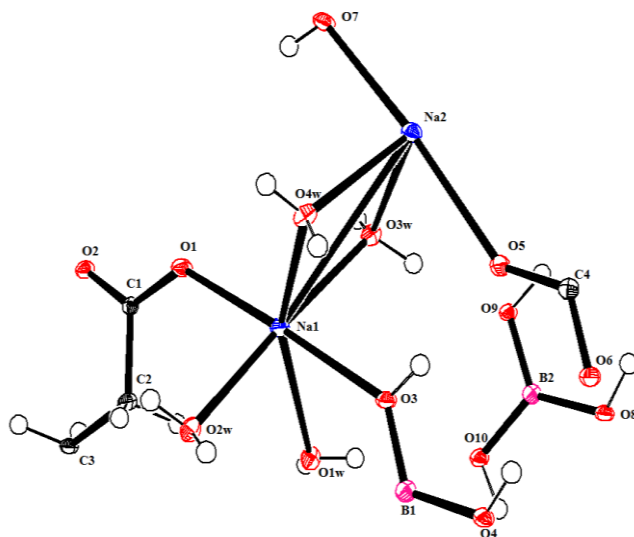

Fig.2 ORTEP diagram of NaBS

By using single crystal XRD data some fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. The molecular weight of the grown crystal is M=357.78, and total number of valance electron Z=70. The grown crystal density was found to be ρ=1.637 g.cm^{-3} and dielectric constant at 1 MHz was calculated as ε_∞ = 23.08. The valence electron plasma energy $\eta\omega_p$ is given by

$$\hbar\omega_P = 28.8\sqrt{\frac{Z\rho}{M}} \tag{1}$$

where, Z is the total number of valence electrons, ρ is the density and M is the molecular weight of the NaBS single crystal. The Plasma energy in terms of Penn gap and Fermi energy [17] is given as

$$E_p = \frac{\hbar\omega_P}{(\varepsilon_{00}-1)^{1/2}} \tag{2}$$

where ε_∞ - dielectric constant at 1 MHz
And

$$E_F = 0.2948(\hbar\omega_P)^{4/3} \tag{3}$$

Polarizability, the value of α is obtained using the relation

$$\alpha=\left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^{-1} \tag{4}$$

where S_o is a *constant* for a particular material and is given by

$$S_0 = 1 - \left[\frac{E_F}{4E_F}\right] + \frac{1}{3}\left[\frac{E_F}{4E_F}\right]^2$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation which is given by

$$\alpha = \frac{3M}{4\pi N_a \rho}\frac{\varepsilon_{00}-1}{\varepsilon_{00}+2} \tag{5}$$

where, the symbols have their usual meaning, N_a is Avagadro number and the fundamental data calculated on the grown crystal of NaBS are listed in Table 1.

Table 1

Fundamental data on various parameters of the crystals formed

S.No	Parameters	values
1.	Plasma energy (eV)	16.30
2.	Penn gap (eV)	3.47
3.	Fermi gap (eV)	12.18
4.	Polarizability (cm^3) Penn analysis	7.35x10^{-23}
5.	Polarizability (cm^3) Clausius-Mossotti Equation	7.87x10^{-23}

3.2. UV-VIS Spectral analysis:

The UV-Vis absorption spectrum of the crystal grown in the lab was carried out between 190 nm to 500 nm using lambda 25 spectrophotometer. The spectrum is taken in the speed of 120 nm/ min with a data interval 1.0 nm as shown in Fig. 2. High transparency in the considered region of wavelength is preferred for optical fabrication.[18] [3]. Optimum transmittance of the crystal in the entire visible region suggests its appropriateness for second harmonic generation (SHG). The UV absorption edge wavelength 244 nm. The band structure and nature of electrons transition study is feasible due to the dependence of optical absorption coefficient on photon energy.
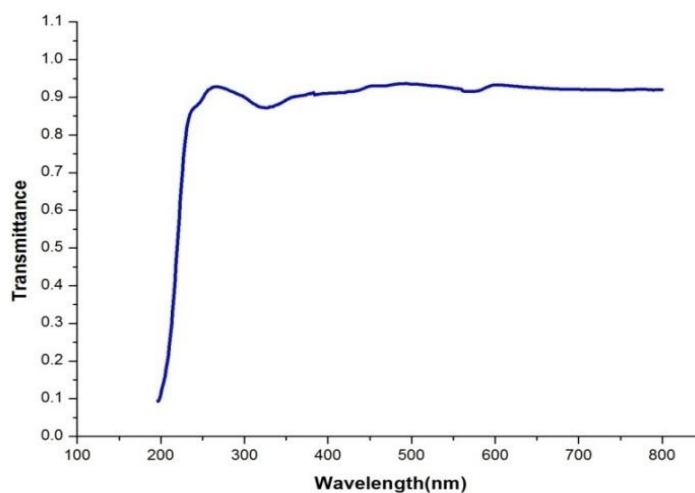

Fig 2 The UV-Vis absorption spectrum of the NaBS crystal

The spectrum demonstrates a very low absorbance in the entire visible region. Sufficient transparency of about 85% with lower cut off wavelength 244 nm was observed. This is the most opted properties for optical device fabrications.

3.3. Thermal analysis:

Thermal stability of NaBS was carried out using thermo gravimetric (TG) and differential scanning calorimetric (DSC). The thermal analysis was carried out by the SDT Q600 V20.9 Build 20 analyzer at a temperature between 50 and 1000 °C at a heating rate of 10°C/min in nitrogen atmosphere. The TGA-DSC curve is furnished in Fig 3.
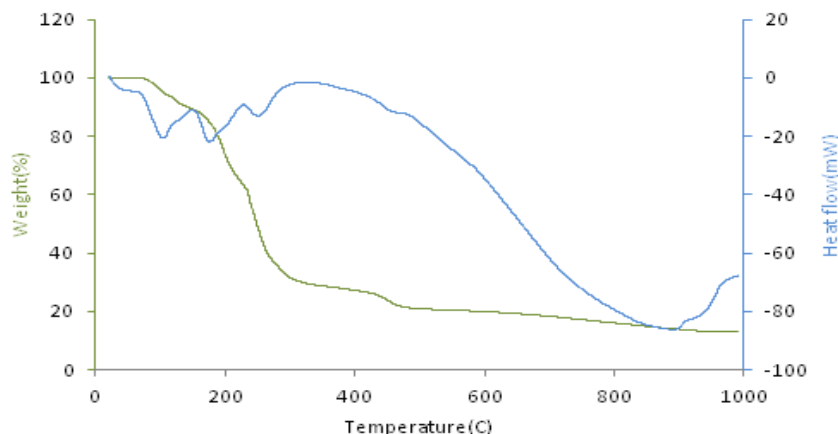
Fig 3 The thermal stability of NaBS crystals using TGA-DSC.

The results of percentage weight loss of the material represent two steps decomposition. The first decomposition commences at 100 °C and ends at 300 °C. This depicts good thermal stability of the material up to 100 °C. The second decomposition takes place at 325 °C with the elimination of 86.87% material into gaseous products. From the TG curve, it is inferred that the various gaseous products evolved are CO_2, hydrocarbon gases. The residual mass of 13.13% after complete decomposition in the crucible might constitute to carbon mass. It is further observed that the DSC curve shows first endothermic peak at around 103.83 °C which is assigned to melting point of the material and a second and third endothermic peak at 177.10°C and 255.07°C which is attributed to the removal of the succinate ion, borate groups and sodium expelled from the compound respectively.

3.4. Laser damage threshold study:

For a novel material, laser damage threshold studies play an important part. Because normally damage of crystals occurs when high intensity power beam falls on it. The LDT value was measured using method Q switched high energy Nd:YAG laser(Quanta ray model lab-170-10) with pulse width(τ) of 6 ns and repetition rate of 10 Hz operating in TEM00 mode. The energy per pulse of 1064 nm laser radiation attenuated using appropriate neutral density filters was measured using an energy meter (EPM 2000, J-50-MB-YAG) which is externally triggered by Nd:YAG laser. For both single and multiple shots experiments, the sample was mounted on X–Y translator. For surface damage, the NaBS crystal was placed at the focus of a plano-convex lens with focal length of 15 cm. The laser beam with diameter of 2 mm was focused on the crystal. An attenuator was used to vary the energy of the laser pulses with a polarizer and a half wave plate.

The pulse energy of each shot was measured using the combination of a phototube and an oscilloscope. The surface damage threshold of the crystal was calculated using the expression:

Power density: $(P_d) = E / \tau \pi r^2$, where E is the input energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). The measured laser damage threshold value of NaBS is 6.34 GW/cm^2 for 1064 nm Nd:YAG laser radiation.

3.5. Dielectric studies

Dielectric constant is one of the essential electrical properties. Dielectric properties have also been correlated with electro-optical property of the crystal. Using parallel plate capacitor (HIOKI-LCR HITESTER 3535) with frequency range 50 Hz to 5 MHz at various temperatures ranging from 313 k to 323 k, capacitance (C_{crys}) and dielectric loss (tan δ) were measured. During sample cooling, the observations were recorded and the dielectric constant was measured by taking the average capacitance (C_{crys}). Fig.4. represents the variation in dielectric constant as a function of frequency.
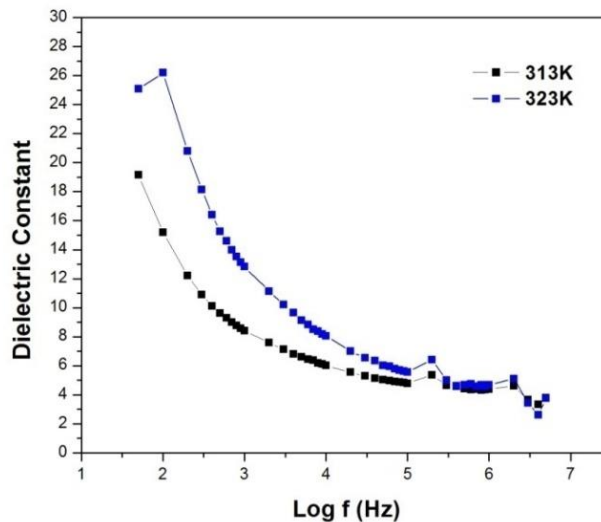

Fig 4 The NaBS crystals have higher value of dielectric constant at lower frequencies

The dielectric studies of NaBS crystals were performed by selecting high transparency and to obtain a good conductive surface layer, the sample is coated with silver paste. The graph demonstrates higher value of dielectric constant at lower frequencies which gradually decreases with increase in frequency. This decrease in dielectric constants at higher frequencies might be due to absence of space charge polarization near the grain boundary interface [19].

Low dielectric loss (tan δ) is preferable for NLO applications. From the graph, it is clear that at high frequencies, very low dielectric loss is observed in NaBS crystal which holds the potent NLO applications [20]. The graph is shown in Fig.5.
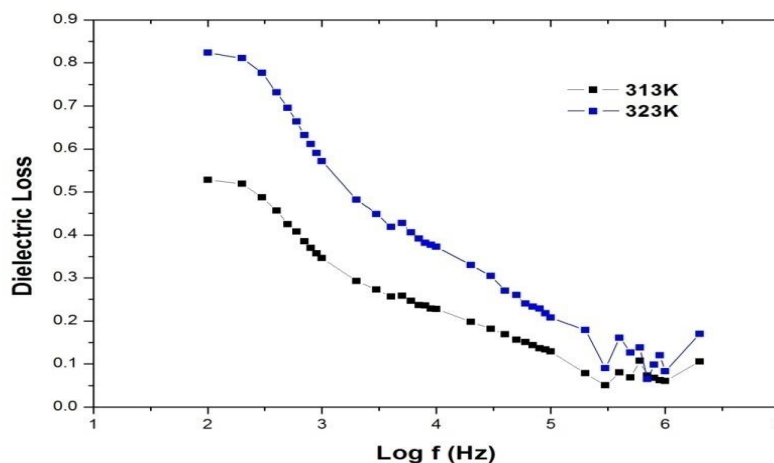

Fig: 5 At high frequencies, very low dielectric loss is observed

3.6. Third order nonlinear optical and optical limiting studies

The Z-scan is a simple and popular experimental technique to measure the intensity dependent third order nonlinear susceptibility of the materials. It allows the simultaneous measurement of both the nonlinear refractive index and the nonlinear absorption coefficient [21]. In this method, the sample is translated in the Z-direction along the axis of a focused Gaussian beam from the He-Ne laser at 632.8 nm and the far field intensity is measured as a function of the sample position. The focal length lens is 18.5-cm. The laser beam waist at the focus is measured to be 15.84 μm and the Rayleigh length is 1.48 mm. 1 mm wide optical cell containing the NaBS sample in DMF is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The experimental result indicates that the sample exhibits saturation absorption with a positive absorption coefficient (β). The maximum transmittance at the focus (Z = 0) reveals the saturation of absorption at high intensity. For materials with saturation of absorption, there is a maximum transmittance in focus at peak and for materials with reverse saturable absorption there is a minimum transmittance in the focus at valley. A peak in the open-aperture curve confirms the occurrence of multi photon absorption in the NaBS Fig.6(a).
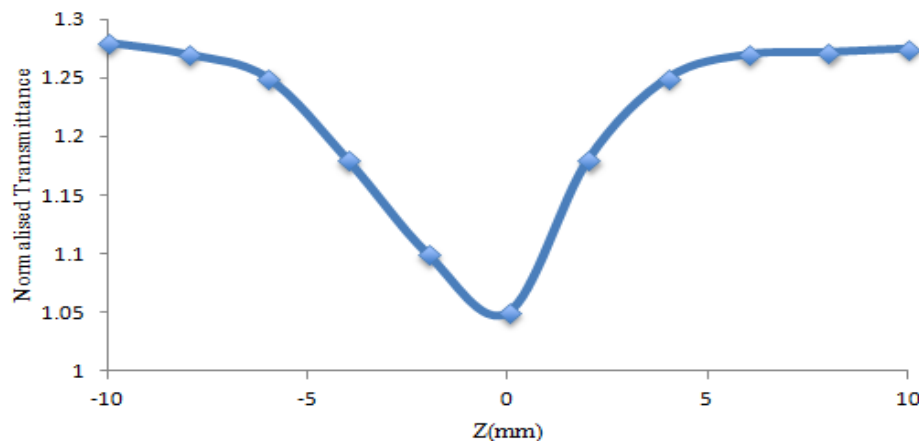
Fig.6(a) Open aperture curve

The peak followed by a valley in the closed-aperture mode Z-scan curve as shown in Fig. 6 (b) indicates the signature of negative nonlinearity due to the self-defocusing effect.
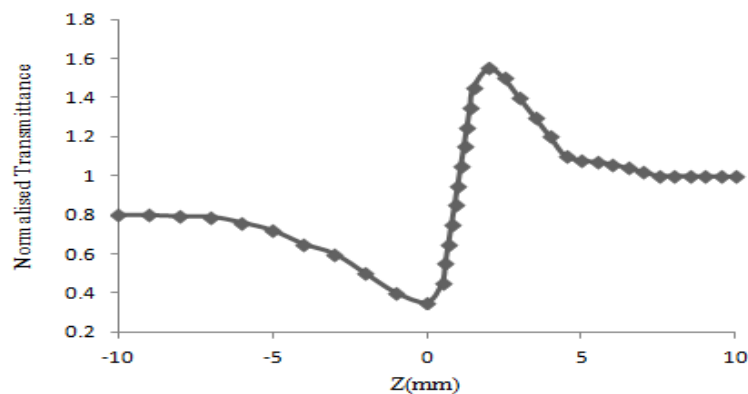

Fig. 5 (b) Closed aperture curve

The third order nonlinear optical parameters were calculated using standard equations. [22-24]. The nonlinear refractive index (n_2), absorption coefficient (β) and third order susceptibility ($\chi^{(3)}$) values of NaBS are calculated to be $5.36 \times 10^{12} cm^2/W$, 4.24×10^{-4} cm/W and 3.5×10^{-4} esu respectively.

4. Conclusion

For the first time, a single crystal of NaBS, a semi-organic NLO material was grown by slow evaporation method. The lattice parameters and the basic parameters of the NaBS crystal was analyzed using the XRD data and the crystal

belonged to monoclinic system. The optical properties such as UV-Vis in transmittance mode and the cutoff wavelength was found to be 244nm. From thermo gravimetric (TG) and differential scanning calorimetric (DSC) analysis, NaBS thermally stable up to 100°C. The measured laser damage threshold value of NaBS is 6.34GW/cm^2 for 1064 nm Nd:YAG laser radiation. Dielectric studies confirm this Crystal is a suitable candidate for NLO applications. The third order nonlinear optical susceptibility, nonlinear refractive index and nonlinear absorption coefficient were determined by Z-scan technique.

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