Growth, Optical, Electrical, Photoluminescence, Thermal and Mechanical Studies of Salicylic acid Single Crystal

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Abstract: Block crystal of salicylic acid (SA) was grown by slow evaporation method. The crystal has very good optical transmittance of 99% throughout the visible and near infrared region. Optical parameters like transmittance, absorbance, reflectance, optical absorption coefficient, refractive index, extinction coefficient, electrical conductivity, optical conductivity and band gap energy of the crystal was calculated from UV-Vis-NIR spectrum. The photoluminescence study indicates the violet emission at 375nm. The thermogravimetric analysis shows that the material is stable up to 160ºC. Mechanical study was carried out using Vickers micro hardness to find the work hardening coefficient, yield strength and elastic stiffness constant of the crystal. The work hardening index (n) is less than 2 indicate that the crystal belongs to hard material. Laser damage threshold of SA crystal has been measured using Nd: YAG laser with the wavelength of 1064 nm. The laser damage threshold value was found to be 15 GW/cm^2.

KEYWORDS: Band gap, Photoluminescence, Thermogravimetric Analysis, Mechanical behavior, Elastic stiffness

1. INTRODUCTION

The search of novel organic materials with prominent optical properties are continuing decades even though many research articles highlighting the results of organic materials possess excellent optical properties. Crystals which possess very good optical properties are being used in the field of photonics, fabrication of LED's, lasers, optical communication, lenses, coatings, solar collectors and reflectors [1]. One of the interesting features of the organic materials is that the chemical structure of the molecular compound can be tuned to get the desired emission wavelength [2]. Organic molecules are preferred due to the much greater design flexibility which allows fine tuning of the microscopic properties and thus the linear and nonlinear optical behavior of the materials [3]. Organic materials can also have narrow band absorption, one can re-orient their optical axis, and they can display bistable electronic states of different spin symmetries. This diversity makes molecular compounds suitable for specific target areas in light-control applications. In addition, organic molecules have favorable mechanical and thermal properties, which allow them to be used for a wider range of optical applications [4]. In this research work we have grown block crystal of salicylic acid and its linear optical behaviors are screened using linear optical characterization techniques. The crystal exhibits excellent optoelectronic properties.

2. EXPERIMENTAL

Salicylic acid purchased from ISOCHEM was dissolved (5g) in acetonitrile without further purification. The clear colorless solution obtained was stirred using magnetic stirrer for one hour at a temperature of 24ºC. The clear solution obtained was filtered using Whattman filter paper and the mouth of the beaker was closed using silver paper. Minute holes were made on the silver paper to pave slow evaporation of the solution. Colorless block crystals were collected after two weeks. Fig 1 shows the block crystal of salicylic acid. The chemical diagram of salicylic acid is shown in Fig 2.

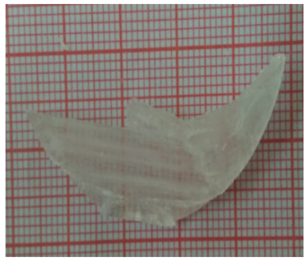

Fig.1- Salicylic acid crystal

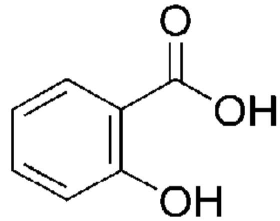

Fig.2- Chemical diagram of salicylic acid

3. RESULTS AND DISCUSSION

3.1. Optical studies

3.1.1 UV Vis NIR Transmission studies

The optical behaviour of salicylic acid crystal was analyzed using UV-Vis NIR spectrometer in the wavelength range of 200-1000 nm. Single crystal of thickness 0.01mm was used for this study. The optical transmittance depends on absorption coefficient (α) [5]. The crystal shows good transparency in the entire visible and infrared region. The cutoff wavelength is observed at 350 nm. Fig 3 shows the optical transmittance spectrum of salicyic acid crystal.

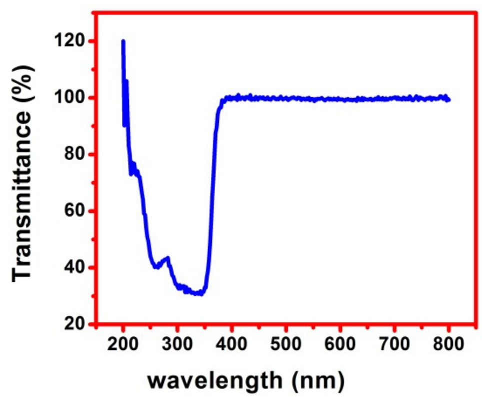

Fig.3- Optical transmission spectrum

3.1.2 UV-Vis Absorption spectral analysis

The UV-Vis spectrum gives valuable information about the atomic structure of the molecules, because the absorption of UV and visible light involves the promotion of σ and **π** orbital electrons from the ground state to higher energy state. The absorption cutoff wavelength of salicylic acid crystal was found to be 380 nm in Fig 4. The optical absorption spectrum indicates that the crystal has lower cut off wavelength of about 380 nm. From the absorption spectrum, it is observed that there is less absorbance in the entire visible and near-infrared region. The wide transparency and lower cut off wavelength is one of the requirements for materials having efficient NLO character [6]. The absorption due to electronic transition above 300 nm is the key requirement for frequency doubling using diode and solid state laser [7]. The absorption peak at 390 nm is assigned to π to π^* transition of the compound. The low absorption edge is necessary for optoelectronic device fabrication [8].

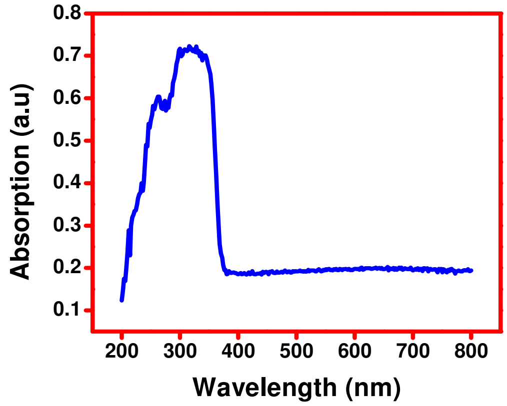

Fig.4- Optical absorption spectrum

3.1.3 Optical band gap energy (E_g) Calculation

For optical device fabrication, the crystal should have high transparency in considerable range of wavelength [9]. The optical absorption coefficient (α) was calculated using the transmittance spectra by the following relation.

$$\alpha = \frac{2.3036 \log(\frac{1}{T})}{d}$$

Where d is thickness of the crystal and T is the transmittance. Absorption coefficient (α) obeying the following relation for high photon energies (hν).

$$h\nu = \frac{1240}{\lambda}$$

The band gap energy was calculated using the following relation [10].

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

Where E_g is the optical band gap of the crystal and A is a constant. The variation of $(\alpha h\nu)^2$ versus hν in the fundamental absorption region are plotted in the Fig 5.The band gap energy is found to be 3.69 eV.

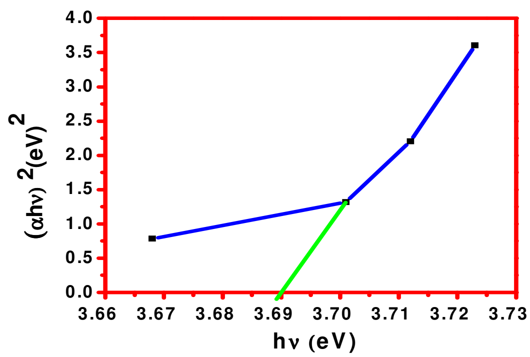

Fig.5- Plot of hν vs $(\alpha h\nu)^2$

3.1.4 Optical constants

The optical behaviour of the materials is important to determine their usage in optoelectronic device fabrication [11]. The study of optical constants of a material such as refractive index and extinction coefficient are quite essential to examine the materials potential optoelectronic applications [12]. The optical constants (n,k) were determined from the transmission (T) and reflection (R) spectrum based on the following relation.

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)}$$

Where t is the thickness and R is the reflectance. Extinction coefficient (k) is the fraction of light loss due to scattering and absorption per unit distance in a participating medium T. The extinction coefficient K can be calculated using the following relation.

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

Where α is the optical absorption coefficient, λ is the wavelength. The plot of extinction coefficient wavelength versus wavelength is shown in Fig 6.

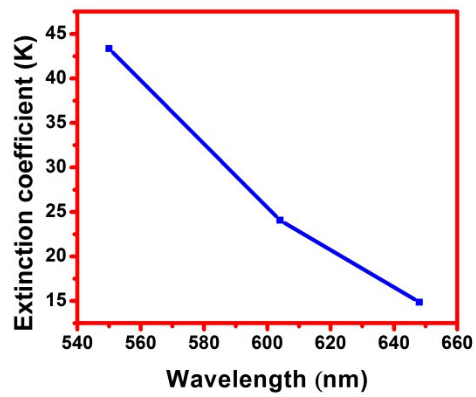

Fig.6-Plot of wavelength vs extinction coefficient

The reflectance (R) gives the ratio of the energy of reflected to incident light from the crystal. The reflectance R in terms of absorption coefficient (α) and the thickness of the crystal (t) can be determined using the relation

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

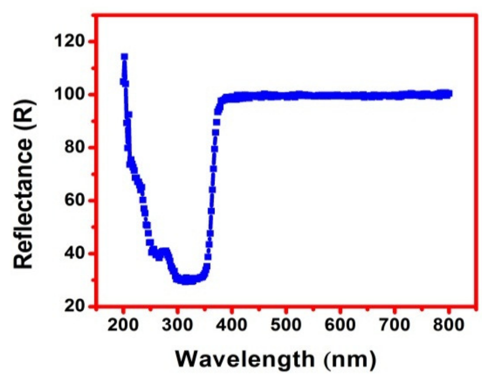

Fig.7-Plot of wavelength vs reflectance

Reflectance as a function of wavelength is shown in Fig 7. Refractive index n can be determined from reflectance data using the equation [14].

$$n = \frac{-(R+1)\pm\sqrt{-3R^2+10R-3}}{2(R-1)}$$

The calculated refractive index (n) using the above equations for the grown salicylic acid crystal is 2.58. The plot of wavelength versus refractive index is shown in Fig 8. The refractive index of the material decreases as the wavelength increases is one of the important parameter for optoelectronic device fabrication.

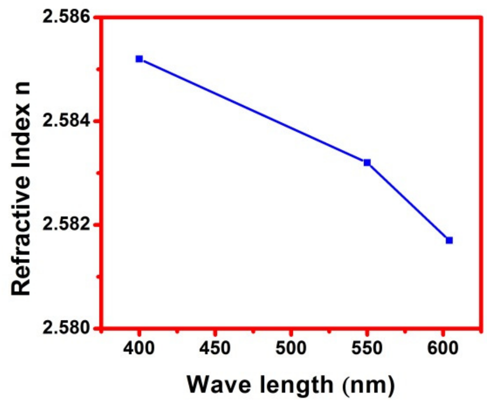

Fig.8- Plot of wavelength vs refractive index

3.1.5 Optical conductivity

The optical response of a material is studied in terms of the optical conductivity. Optical conductivity is one of the powerful tools for studying the electronic states in materials [15]. It has dimensions of frequency which are valid only in a Gaussian system of units. The optical conductivity (σ_{op}) has been determined from the relation

$$\sigma_{op} = \alpha nc/4\pi$$

Where c is the velocity of light, α is the optical coefficient and n is the refractive index.

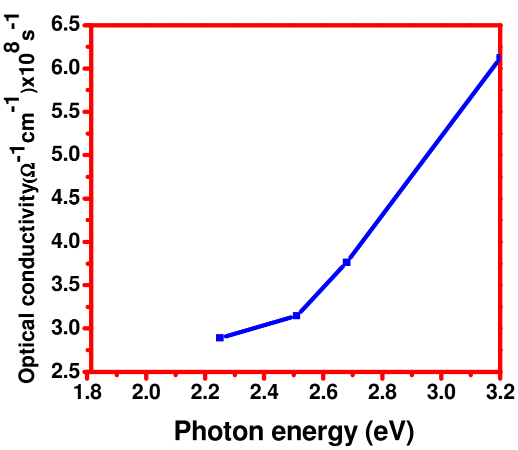

Fig.9- Plot of energy vs optical conductivity

The optical conductivity of salicylic acid increases with increase of photon energy as in Fig 9 indicates the very good optical response of the material. The variation of optical conductivity with wavelength is shown in Fig 10. The higher value of optical conductivity (10^9-10^{12}) shows the very good photo response of the crystals [16].

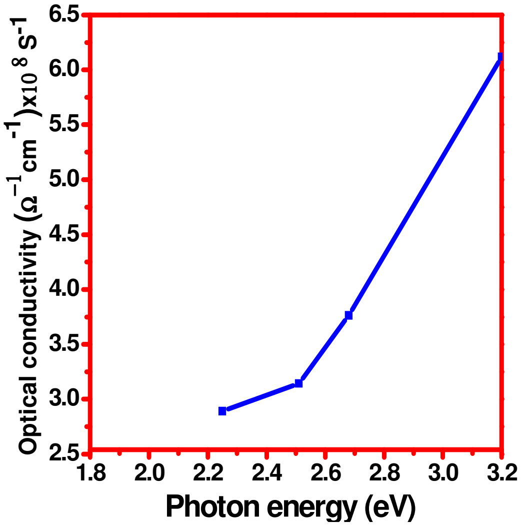

Fig.10- Plot of Wavelength vs optical conductivity

3.1.6 Electrical Conductivity

The value of electrical conductivity of a material is related with the optical conductivity value of the crystal using the following equation.

$$\sigma_e = 2\lambda\, \sigma_{op}/\alpha$$

The electrical conductivity of the material decreases with increase in the photon energy as shown in Fig 11.

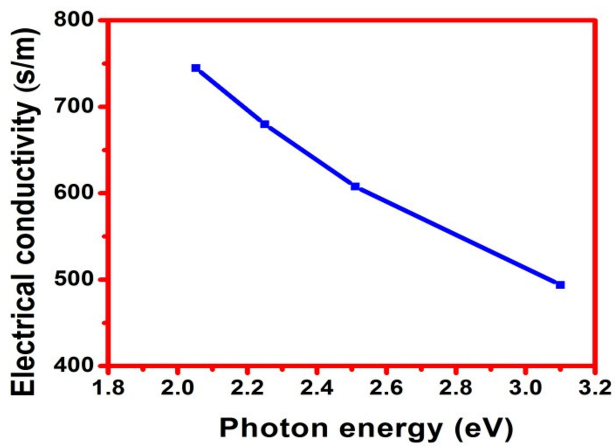

Fig.11- Plot of energy vs electrical conductivity

3.1.7. Electric Susceptibility

Electric Susceptibility is defined as the ratio of polarization (p) to the average electric field (E). The electric susceptibility (χ_c) can be calculated from the following relation [17, 18].

$$\varepsilon_r = \varepsilon_0 + 4\pi\, \chi_c = \eta^2 - k^2$$

$$\chi_c = \eta^2 - k^2 - \varepsilon_0/4\pi$$

Where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The complex dielectric constant is given by ε_c.

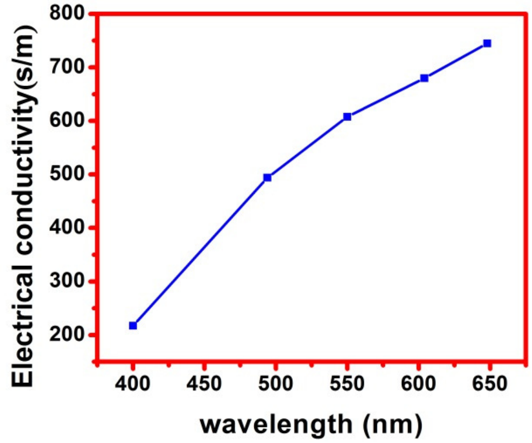

Fig.12- Plot of wavelength vs electrical conductivity

The real and imaginary part of dielectric constant from extinction coefficient is given as [19, 20]

$$\varepsilon_c = \varepsilon_r + \varepsilon_i$$
$$\varepsilon_r = n^2 - K^2$$
$$\varepsilon_i = 2nK$$

Where ε_r and ε_i are real and imaginary part of dielectric constant. The electric susceptibility is calculated as $\chi_c = 0.5199$.

3.1.8 Determination of Urbach energy

The linear absorption coefficient (α) of the material is related to the Urbach energy by the relation [21].

$$\alpha = \alpha_0 \exp(h\nu/E_u)$$

Where α_0 is a constant and E_u is the Urbach energy, which is a measure of signal depth of tail levels stretching in to the forbidden electronic band gap below the absorption edge. The value of Urbach energy (E_u) was determined by the reciprocal of the slope of the linear portion of the plot drawn between α versus photon energy (hν) shown in Fig 13.

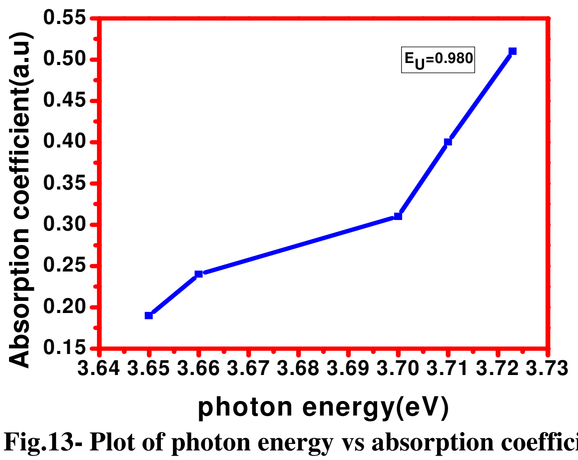

Fig.13- Plot of photon energy vs absorption coefficient

The estimated value of Urbach energy for salicylic acid crystal is found to be 0.980 eV. This is low value which predicts that the grown crystal has highly crystalline in nature with fewer disorders in the near band edges [22].

3.1.9. Determination of Steepness parameter (σ_s) and strength of electron phonon interaction

Steepness parameter is interpreted as the ratio of wave height (H) to the wavelength (λ). It is basic and very important parameter for the nature of interaction between the photon and electrons. The steepness parameter which is in correlation with Urbach energy and highly depends on temperature of the system can be calculated using the relation,

$$\sigma_s = K_B T / E_u$$

Where E_u is the Urbach energy (0.980 eV), K_B is the Boltzmann's constant 8.6173 x 10^{-5} eV and T is the absolute temperature. Further, the strength of electron and phonon interaction in terms of steepness parameter could be expressed [23],

$$E_{e\text{-}p} = 2/3\ \sigma_s$$

The estimated value of steepness parameter and strength of electron-phonon interaction is found to be 0.0240 eV and 27.77 eV^{-1}. In general, the electron-phonon interaction parameter value greater than 10 is considered as a high value. For analysis the value of electron-phonon interaction is 13.58 eV^{-1} and 0.0491 eV for the reported crystals, namely 2-amino-5-methyl-pyridinium trifluoroacetate [22, 24]. The high value of electron –phonon interaction parameter indicates the perfect optical density of this compound.

3.2. Photoluminescence

Photoluminescence spectroscopy is the standard technique for characterizing defects, vacancies and other imperfections existing in the crystal [25, 26]. The behavior of photo-induced electron-hole pair, charge separation and charge recombination process can be understood by this technique [27, 28]. The Photoluminescence studies were carried out for the crystal at the room temperature in the wavelength range of 300 to 550 nm. The excitation peak is observed at 348 nm.

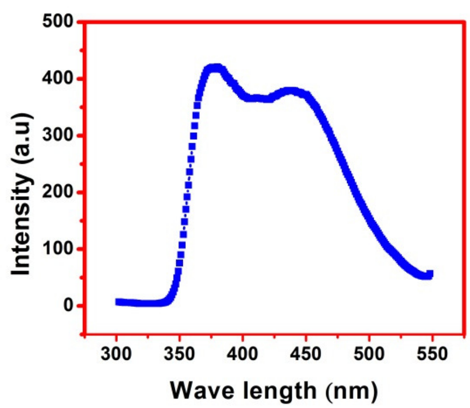

Fig.14- Photoluminescence spectrum of salicylic acid

The emission peak observed at 375 nm in Fig 14.indicates that salicylic acid crystal has violet fluorescence emission. The band gap energy of the crystal was calculated using the relation 1240 /λ and E_g= 3.30ev.

3.3. Thermal Studies

3.3.1. TGA/DSC

Thermal analysis is used to find out the weight loss (TGA) and (DSC) thermal stability of the grown crystal with respect to the temperature. The TGA curve gives the quantitative measurement of mass change associated with the transition. The thermal stability of salicylic acid crystal was screened by Perkin-Elmer Thermo Gravimetric analyzer (TGA) with Differential Scanning Calorimetry (DSC) in the air atmosphere with a heating rate of 2ºC / min with the temperature range of 50 ºC to 450 ºC as shown in Fig 15. The salicylic acid crystal is stable up to 160 ° c and loss in mass is observed on further heating. TGA curve shows single stage weight loss patterns is observed from 145^0c up to 225^0c and it is approximately 100 percentage loss of the compound. The TGA curve indicates that the sample is stable up to the temperature of 145^0c, indicates the material is suitable for optoelectronic applications [29]. In the DSC curve the first endothermic peak is observed at 160^0 c indicates the melting of the crystal and the decomposition of the material is confirmed by the second endothermic peak observed at 225^0 c.

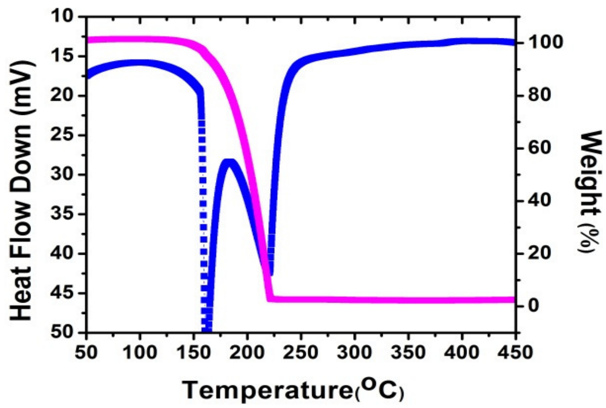

Fig.15- TGA/DSC of salicylic acid

3.4. MECHANICAL STUDIES

3.4.1. Micro hardness studies

The micro hardness of salicylic acid crystal was determined by Vickers's micro hardness test for the static indention test load varying between 10g to 100g were applied on the grown crystal using diamond pyramid indenter connected to an incident ray research microscope. An average of at least three impressions was recorded for each load with a dwell time of 10s. The calibration microscope attached to the system has measured the diagonal length (d) of the indentation mark after unloading. It was calculated using the formula.

$$H_v= 1.8544p/d^2 \text{ kg /mm}^2$$

The plot of load vs hardness values are shown in Fig 16.

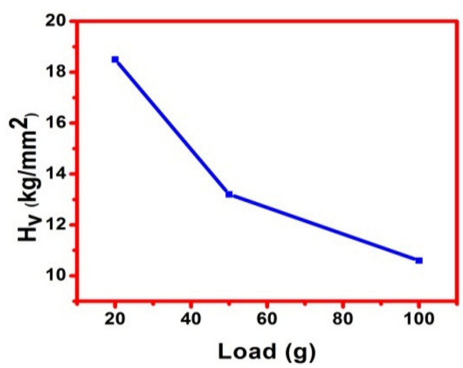

Fig.16- Plot of load vs H_v

The hardness value decreases with the increase in load, which indicates that salicylic acid is exhibiting normal Indentation size effect (ISE). When the applied load is small the indenter penetrates only on an upper surface layer of the crystal and depending on the strain distribution of upper layer there is fall of hardness value in low load region. As the load increases the depth of indenter increases and both the effects of the inner layer and surface layer contribute to the less hardness value [30].The knoop intended impressions was approximately rhombohedral shape. Average diagonal length (d) was considered for the calculation of knoop micro hardness number H_k using the relation [31].

$$H_k = 14.229p/d^2 \text{ kg /mm}^2$$

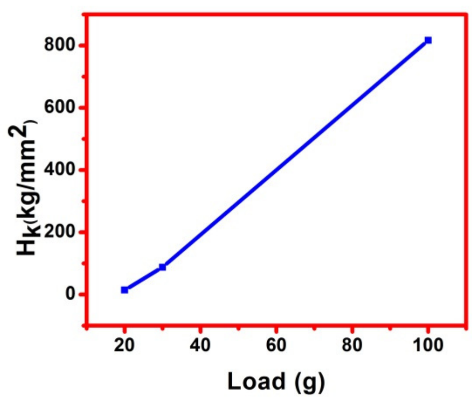

Fig.17- Plot of load vs H_k

Where p is applied load in kg, and d is in mm and H_k is a kg/mm^2. The Mayer's index number was calculated from the Mayer's law which relates the load and indentation diagonal length

$$np = kd, \log p = \log k + \log d$$

Where k is the material constant and n is Mayer's index or work hardening coefficient. The above relation indicates that H_v should increase with the increase in p if n>2 and decrease with p when n<2.

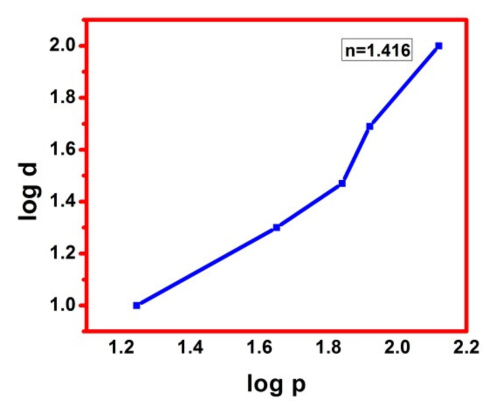

Fig.18- Plot of log p vs log d

The n value was determined from the plot of log p and log d will give the work hardening index (n). This is found to be 1.416. According to Hanneman [32].The value of n is less than 2 for hard materials. And more than 2 for soft ones. Thus salicylic acid crystal belongs to the hard material category. The yield strength σ_y of the material has been studied using the following relation

$$\sigma_y = H_v/3$$

The bonding nature of the material has been determined by elastic stiffness. The elastic stiffness constant C_{11} of the material can be calculated from Wooster's expression.

$$C_{11} = H_v^{7/4}$$

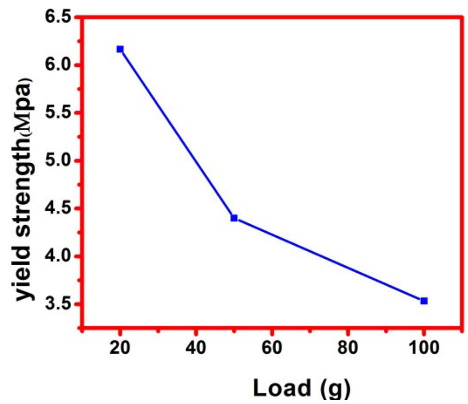

Fig.19-Load vs yield strength

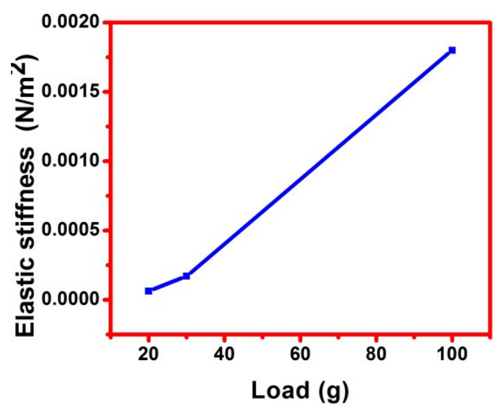

Fig.20- Plot of load vs elastic stiffness

From the Fig 19 and 20 the yield strength and elastic stiffness constant of the material is found to be increase with increase load which implies that salicylic acid has high mechanical stability by using above relation.

3.5 Laser Damage Threshold (LDT) studies

Laser damage threshold (LDT) studies the optical crystal efficiency is proportional to the fundamental laser beam power density. Because of changing the power density leads to produce optical materials breakdown. For device fabrication, high energy surface damage resistant is the most important property [33, 34]. The LDT value of a material depends upon optical absorption and specific heat, etc. The fat and defect-free crystal was used for LDT measurement. Clear visible damage occurred when the input laser energy reaches 7.5 mJ for KDP (Reference) crystal. The laser damage threshold resistant of the grown crystal was estimated using the equation [34, 35],

$$\text{Power density } P_d = E_p / \tau \pi (\omega_o)^2$$

Where E_p is the laser beam input energy (mJ), τ is the laser pulse width (ns) and ω_o is the beam waist radius at focal (cm) and it was determined by the relation:

$$2\,\omega_o = (4\lambda/\pi)\,(f/d)$$

Where λ is the laser wavelength (1064 nm), f is the convex lens focal length (10 cm) and d is the laser beam diameter (1 mm). The calculated value of ω_0 is 0.6775m. The laser damage threshold value was found to be 131 mJ (1.5508x10^-14 W/cm^2) or (15.5086 GW/cm^2). The laser induced damage occurs in a crystal due to its optical behavior and material defects, impurities and surface roughness behavior [36].

CONCLUSION

Block transparent single crystal of salicylic acid was grown from acetonitrile solvent by slow evaporation method. From the recorded UV-Visible spectrum, 99% transparency was observed. The energy band gap was found to be 3.69 eV from the Tauc's plot. The refractive index, extinction coefficient, reflectance, optical conductivity, electrical conductivity, and electrical susceptibility of the crystal were calculated. TGA/DSC confirms the thermal stability of the crystal up to 160º c. Photoluminescence spectral analysis shows the violet emission of the crystal. The work hardening index (n) is less than 2 indicate that the crystal belongs to hard material. The laser damage threshold value was found to be 15 GW/cm^2. The wide band gap, very good transparency, thermal stability of the material up to 160 º c, violet emission and the hardness of the material indicates the suitability of the material for optoelectronic applications

REFERENCES

1 Manthos Papadopoulos G, Andrzej Sadlej J, & Jerzy Leszczynski, *Nonlinear optical properties of matter* (Springer) 1th Edn, 2006 p. 419.
2 Mark Fox, *Optical properties of solids(*Oxford master series in condensed matter Physics. Oxford University) 2th Edn, 2010, p.12.
3 Munn R W, Ironside C W, *Advanced materials,* 5 (1993) 772-773.
4 Manthos Papadopoulos G, Andrzej Sadlej J, & Jerzy Leszczynski, *Non-Linear Optical Properties of Matter from Molecules* to *Condensed Phases Manthos (*Springer, Netherlands) 1th Edn, 2006, p. 2.
5 Sharma P, Katyal S C, *Res. Lett.Mater. Sci*. (2008) 1–4.
6 Amutha M, Raj Kumar R, Thayanithi V. & Praveen kumar, *Advances in optical technologies,* (2015) 206325.
7 Guan XH, Chen GH, Shang C, *J Environ Sci* (China) 19 (2007) 438-443.
8 Jaishree D, Kanchana G, Kesavasamy R, *Condense. Matt. Phys.* (2014) 5–10.
9 Dmitriev V G, Guruzadyan G G, and Nikoyosyan D N, Hand-book of Nonlinear optical crystals, springer, Berlin, Germany, 1999.
10 Tauc J, Grigorovici R, Vancu A, *Phys. Status Solidi B*, 15 (1996) 627-637.
11 V Pandey N Mehta S K Tripathi and A Kumar, *Chalcogenide Letters*, 2 (2005) 39-44.
12 Urbach F, *Molecular and Optical Physics*, 92 (1953) 1324-1325.
13 Dongol M, *Egyption Journal of Solids,* 25 (2002) 33-47.
14 Ashour A, EI-Kadry N, and Mahmoud S A, *Thin solid films*, 269 (2000) 1555-162.
15 Arumanayagam T, & Murugakoothan P, *Journal of minerals & materials characterization & engineering,* 10 (2011) 1225-1231.
16 HiralRaval B B, Parekh K D, Parikh and M J Joshi, Hindawi, *Advances in condensed matter physics,* 9 (2019) 3853215.
17 Gupta V, and Mansingh A, *Journal of Applied Physics,* 80 (1996) 1063-1073.
18 Kochuparampil, A.P., Joshi, J.H. and Joshi M J *Modern Physics Letters B*, 27 (2017).
19 Dhanaraj P, Suthan, T, and Rajesh N, *Current applied physics,* 10 (2010) 1349-1353.
20 Dongal M, *Egyptian Journal of solids*, 25 (2010) 33-47.
21 Urbach F, *Phys Rev,* 92 (1953) 1324.
22 Jayaprakash P, Sangeetha P, RathikaThayakumarai C & Lydiacaroline M, *Physica Condens Matter* , 1 (2017) 518.
23 Kandhan S, *Mater. Sci*, 55 (2020) 8591.
24 Kumari C R T, *et al. Crystals* 11 (2021) 1239.
25 Rani N, Vijayan N , Thukral Kanika, Maurya K Haranath D, Bhagavannarayana G, Verma S, Wahab M A, *Spectrochim. Acta Part A* 105 (2013) 192–199.

26 Sakthy Priya S, Alexandar A, Surendran P, Lakshmanan A, Rameskumar P. Sagayaraj P, *Opt. Mater.* 66 (2017) 434–441.
27 Abdullah S A, Sahdan M Z, Nafarizal N, Saim H, Bakri A S, Cik Rohaida C H, Adriyanto F & Sari Y, *Journal of Physics*, 995 (2018) 012067.
28 Chung C K, Liao M W & Lai C W, *Thin solid films,* 5 (2009) 1415-1418.
29 S Sudhakar, M Krishnakumar, A Silamparasan, R Muralidharan *journal of materials* (2015) 260325.
30 H Arul, D Rajan babu and R Ezhil Vizhi, *J.Chem*,(2018) 511-515.
31 Pal T and Kar T *Mater. Lett.*59 (2005) 1400
32 Hanneman, Metall. Manchu, M (1941) 23, 135.
33 K Nivetha, S Kalainathan, M Yamada, Y Kondo, F. Hamada, *J. Mater. Chem. Phys*, 28, (2017) 5180–5191
34 P Karuppusamy, M S Pandian, P Ramasamy, S Verma, *Opt. Mater.* 79(2018) 152–171.
35 Wood R M, Laser-induced Damage of Optical Materials (Institute of Physics Publishing, Dirac House, Bristol, UK, 2003)
36 Silambarasan A, Rajesh, P, Rajeev Bhatt, Indranil Bhaumik, Karnal, AK, Ramasamy, P & Gupta, *Applied Physics A*, 122 (2016) 736.