



Studies on Non-Linear Optical Single Crystal of Alizarine Doped Butylated Hydroxy Toluene (BHT)

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ABSTRACT

Single crystal of alizarine doped BHT was successfully grown by solution method with slow evaporation technique at room temperature. The properties of grown crystal were characterized by different techniques. The parameters of the unit cell were determined by XRD technique. The vibrational frequencies of various functional groups in crystal have been derived from FT-IR analysis. UV-Vis spectral analysis shows the range of optical transmission. By Vickers microhardness method we analyzed the mechanical property of grown crystal.

Key Words: BHT, XRD, FT-IR, UV-Vis, Vickers microhardness

INTRODUCTION

Nonlinear optical materials are used in abundance for telecommunications, electro-optic modulators, high density optical memories, optical bistability, color displays, etc. [1]. Second harmonic generation (SHG) measurements of organic nonlinear optical materials have already produced results, which by far, supersede those obtained from all the known inorganic alternatives. The polar organic materials from symmetric crystal structure gives rise to second-order nonlinear optical properties [2,3]. Organic nonlinear optical materials are often formed by weak Vander Waals and hydrogen bonds and hence possess high degree of delocalization. Organic materials are molecular materials those having unique opportunities for fundamental research as well as for technological applications [4].

Search for a new NLO material with high optical nonlinearity, chemical flexibility, mechanical strength and thermal stability is very essential to fulfill the increasing demand in the field of telecommunication, optical computing and optical data storage. In the nucleation and growth of certain nonlinear optical crystals, amino acids play a vital role. The main reason for enhanced SHG activity in organic materials is the chirality, wide transparency ranges in the visible and UV spectral regions and hydrogen bonds of the material [5].

SAMPLE PREPARATION

BHT was taken for single crystal and was purified by recrystallization process. The BHT crystals were grown from saturated solution by slow evaporation technique [6,7]. Initially single crystal, pure form of BHT in ethanol was grown by slow evaporation method. Good quality single crystals of BHT have been collected from the recrystallization process[8] during the time of 15 days. The photocopy of the grown BHT crystal is shown in Fig. 1.

Single-crystal X-ray Diffraction

The single crystal of BHT has been subjected to X-ray diffraction studies to determine the unit cell parameters and morphology. From the single crystal XRD data for the grown Doped Butylated Hydroxy Toluene (BHT) crystals, it is observed that the BHT crystal belongs to orthorhombic system with the space group of $P2_12_12_1$. It has the following cell dimensions $a = 8.814 \text{ \AA}$, $b = 10.345 \text{ \AA}$, $c = 15.553 \text{ \AA}$ and cell volume $V = 1418.14 \text{ \AA}^3$. The BHT crystal belongs to space group $P2_12_12_1$ which is recognized as non centrosymmetric, thus satisfying one of the essential material requirements for the SHG activity of the crystals.

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FTIR spectrum of doped BHT

KBr pellet technique is used to record the Fourier transform infrared spectrum at room temperature in the range of 4000–400 cm^{-1} . The effect of aligirin on the functional groups of the pure BHT crystal is identified by the FTIR spectrum[9]. The recorded FTIR Spectrum of Doped BHT crystal shown in fig. 2 exactly match with each other due to overlapping of bonds although there is a change in organic elements percentage due to the addition of dopants[10,11]. The frequencies with their relative intensities obtained in FTIR spectrum of dye doped BHT crystal are mentioned in Table 1.

UV-Visible spectrum of doped BHT

The optical properties of the crystals are important since a crystal can be employed for real-time applications only when they are transparent in the wavelength of interest [12]. The UV-Vis-NIR absorption and transmittance spectrum for the BHT crystals was recorded by Shimadzu model 1601. It is observed that BHT has an absorbance varying in the region 200-300 nm[13]. There are no characteristic absorptions observed in the region between 300 and 800 nm, which justifies that the BHT crystal are suitable for optical applications and the spectrum is shown in Fig. 3.

TGA/DTA analysis of doped BHT

The thermo gravimetric analysis deals with the change in the mass of a substance, continuously monitored as a function of temperature when it is heated. The Differential Thermal analysis (DTA) shows the variation of heat flow with temperature. The TGA and DTA analysis of BHT was carried out between 25 - 500°C in air atmosphere at a heating rate of 20°C/min using Netzsch instrument [14,15]. The TGA and DTA curves are shown in Fig. 4. Thermal decomposition of doped BHT crystal begins at 71° C and ends at 170° C. The grown crystal gets fully decomposed at 170° C. A sharp endotherm at about 71.8°C for the grown crystal is due to the melting point of doped BHT crystals. The second endothermic peak at 170°C. In TG analysis the weight loss 98.5% due to evaporation of water molecules present in the crystal between the temperature range between 80°C and 180 °C. After that the sample is stable between the temperature range 180 °C - 500 °C.

Dielectric Analysis

Crystal of doped BHT was selected to measure dielectric permittivity, dielectric loss and A.C conductivity using HIO-KI 3532 -50 LCR HITESTER model 3532-50 LCR meter in the frequency range of 50 Hz and 5MHz at various temperatures [16]. The dielectric constant and dielectric loss of the samples were calculated from capacitance and dissipation factor. The dielectric constant of the doped BHT crystal were calculated through the capacitance by the fundamental equation (1)

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (1)$$

Where C is capacitance is thickness of the sample, $\epsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$ is the permittivity of free space, A is the area of cross section.

The dielectric loss ($\tan \delta$) were calculated by the equation (2)

$$\tan \delta = \epsilon_r D \quad (2)$$

Where D is the dissipation factor. The variation of dielectric constant was measured as a function of frequency at different temperatures for doped BHT crystals shown in Figure 5, while the corresponding dielectric losse are depicted in Figure 6. The very high values of $\tan \delta$ at low frequencies are due to presence of all forms of polarizations namely, space charge, orientation, ionic and electronic polarization. As the frequency increases, the space charge cannot sustain and comply with external field and hence the polarization decreases. According to Miller rule, the low value of dielectric loss at high frequency revealed the high optical quality of the crystal.

The AC conductivity is calculated using

$$\sigma_{ac} = \omega \epsilon_0 \epsilon_r \tan \delta \quad (3)$$

Where, f is the frequency of the applied electric field. The figure 7 shows the variation of AC conductivity for different frequencies. From the graph, it is observed that both the crystals have the AC conductivity feebly increases up to the logarithmic of 6.70Hz. From the sharp increases it was observed in the logarithmic frequency 6.87Hz indicates the dielectric breakdown frequency of the material.

Microhardness Studies

Vickers microhardness indentations were made on as grown crystal surface of the doped BHT crystal at room temperature with the load ranging from 25g, 50g and 100g using Vicker's microhardness tester[17]. The Vickers hardness number was calculated using the expression

$$H_v = \left[\frac{1.8544 P}{d^2} \right] \text{ kg/mm}^2 \quad (4)$$

Where, H_v is the Vickers hardness number in kg/mm^2 , P is the applied load in kg and d is the diagonal length of indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid. A plot obtained between the hardness number and the load is depicted in Figure 8.

Mayer Index (N)

Kick law proposed the relation between load P and indentation length d is given by,

$$P = k_1 d^n \quad (5)$$

Where, n is the Mayer's index or work hardening coefficient which is found out from the slop of the plot of $\log P$ and $\log d$ gives a straight line as shown in Figure 9 and k_1 is the standard hardness, which is found by the intercept [18]. In the present investigation, the work hardening coefficient (n) for doped BHT crystals are $n = 3$ and hence it behaves as a hard material. The material is confirmed as hard material with amount of mechanical strength which is better for device fabrications.

CONCLUSION

Single crystals of BHT have been grown successfully from aqueous solution by slow evaporation method. The variation of lattice parameters has also been calculated from single crystal XRD analysis. The spectral analysis carried out using the FTIR spectroscopy shows the presence of functional groups. Its optical behavior has been assessed by UV-Visible spectroscopy. The thermal behavior of the crystals has been studied by obtaining TGA and DTA studies. Vicker's microhardness reveals that the hardness number H_v increases with increasing load exhibiting indentation size effect. The material suggests that it belongs to hard material category according to Mayer's index number (n).

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Table 1: Vibration modes in BHT crystal

S. No.	Functional group	Wavenumber (cm ⁻¹)
1	O-H stretching	3626
2	C-H stretching (aromatic)	3068
3	C-H ₃ asymmetric stretching	2955
4	C-H ₃ symmetric stretching	2870
5	C=C stretching (aromatic)	1618
6	C-H ₃ bending	1448
7	Tert-butyl group	1396
8	C-H bending (in plane)	1230
9	C-O stretching (C-OH)	1213
10	O-H bending (in plane)	1149
11	C-H ₃ rocking	1026
12	C-C ring stretching	866



Figure 1: Single crystal of doped BHT.

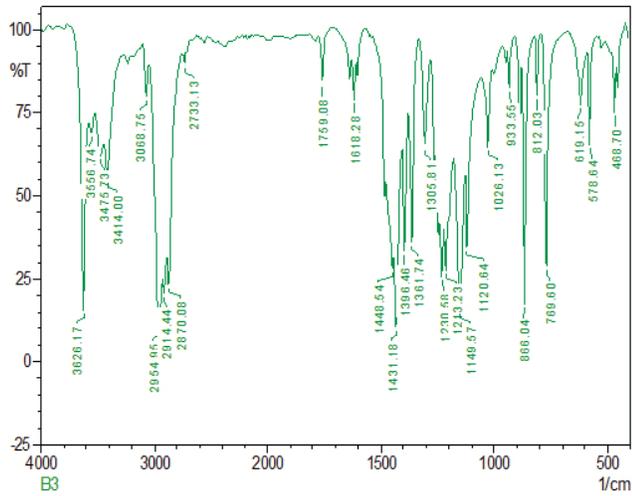


Figure 2: FTIR spectrum of doped BHT.

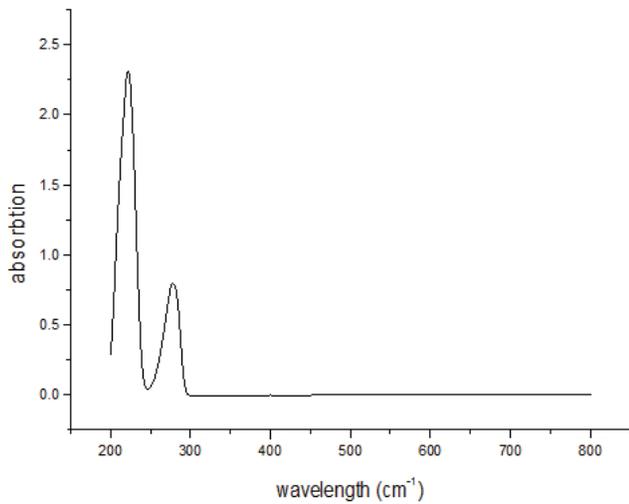


Figure 3: UV-Visible spectrum of doped BHT.

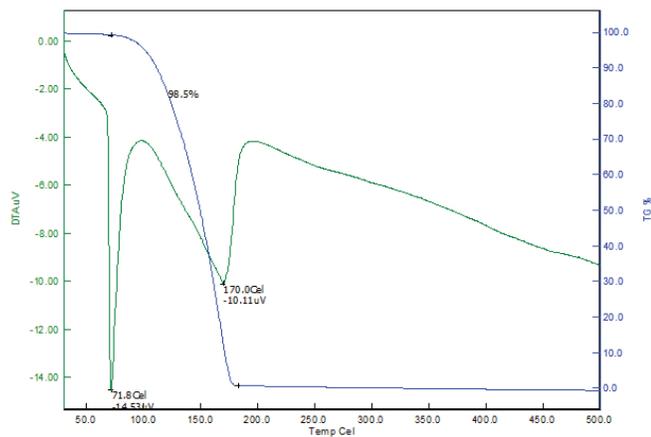


Figure 4: TGA/DTA analysis of doped BHT.

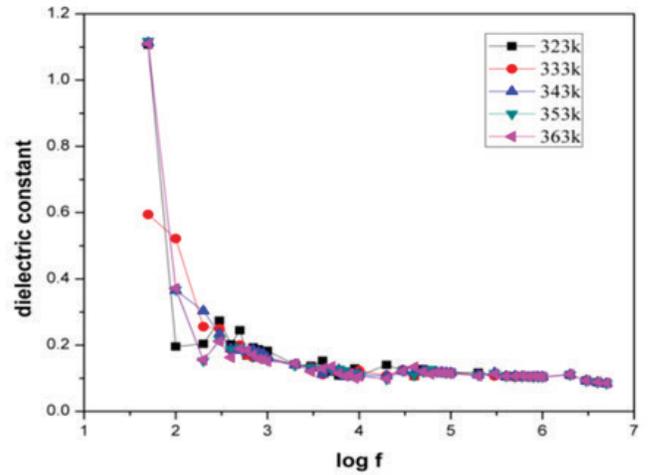


Figure 5: Dielectric constant versus log f doped BHT crystals.

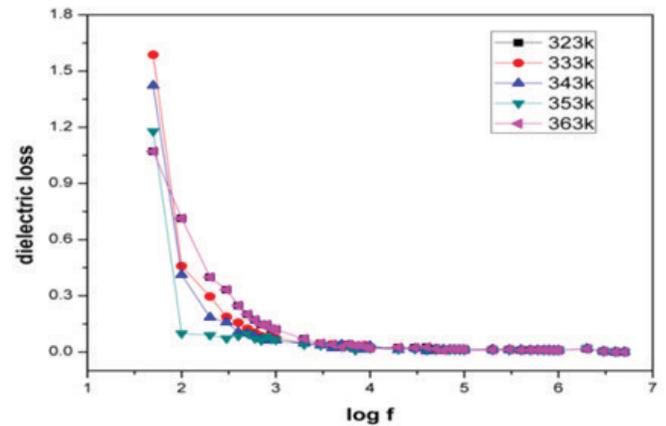


Figure 6: Dielectric loss versus log f for doped BHT crystals.

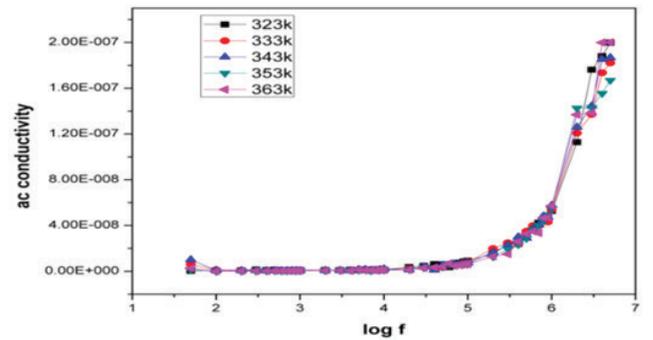


Figure 7: AC conductivity of doped BHT.

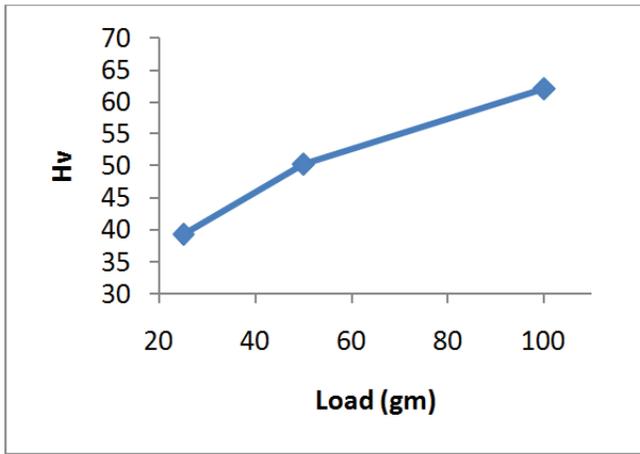


Figure 8: Variation of Vickers Hardness Number with applied load for doped BHT crystals.

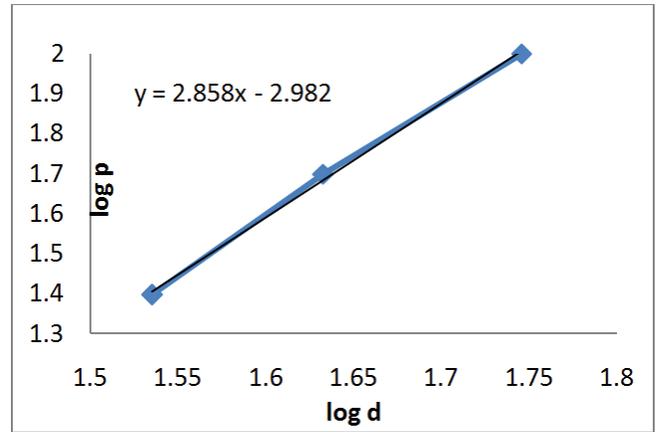


Figure 9: Log P versus log d for doped BHT crystals.