Growth and Characterization of Dye Doped Butylated Hydroxy Toluene (BHT) Single Crystal

R. Raja¹, S. Seshadri², V. Santhanam³

¹Department of Physics, SCSVMV, Kanchipuram 631561, India; ²Department of Physics, Govt. Arts college, Vysarpati, Chennai- 601204, India; ³Department of Chemistry, SCSVMV, Kanchipuram 631561, India

ABSTRACT

Organic Non-linear optical single crystals with the second harmonic generation values are useful in optical communication and signal processing in integrated optics. Rhodamine is a dye, an organic molecule well-studied in laser physics and nonlinear optics for its fluorescent properties. In the present work, a new organic rhodamine dye doped Butylated hydroxy toluene (DBHT) single crystals were grown by slow evaporation technique. The lattice parameters of the grown crystals are found from single crystal XRD analysis. The FT-IR analysis confirms the presence of various functional groups available in DBHT. The dielectric analysis can be used to find the electrical properties of DBHT single crystal as a function of temperature and frequency. The optical studies carried out reveal that the DBHT crystals exhibit good optical quality and possible NLO applications. The thermal and mechanical stability of the crystal is studied by TG/DTA analysis and Vicker's microhardness test.

Key Words: NLO, XRD, Hardness studies

INTRODUCTION

Nonlinear optical materials (NLO) have attracted many researchers due to its wide applications in the field of telecommunication, optoelectronic and optical information storage devices [1-6]. Organic materials are known for their potential applications in semiconductors, superconductors and nonlinear optical devices [7]. Hence, Organic NLO crystals with high second harmonic generation efficiency and transparency in UV-Vis. region are required for numerous device applications. In the present work, single crystals of rhodamine doped BHT crystals are grown by slow evaporation technique.

Rhodamine is a dye, an organic molecule well-studied in laser physics and nonlinear optics for its fluorescent properties. Solutions of this dye are commonly used in biology as a staining fluorescent dye for optical microscopy and in optical applications to provide laser gain media. Dyeing of crystals is a practice developed particularly for quantum optics applications, because of the very significant increase in surface area achieved in growing crystals[8]. The grown crystals were subjected to various characterizations such as

single crystal XRD, FTIR, UV, NLO, dielectric studies, thermal and mechanical analysis and the results are discussed in detail.

Crystal Growth

Anal grade of BHT are dissolved in ethanol and the solution is stirred continuously about 5 hrs. The saturated solution is filtered and kept safely with tightly closed plastic cover. Good optical single crystals of BHT are collected from the solution in 15 days of time[9]. The saturated solution of BHT is mixed with 0.01 M% of rhodamine B. The mixed solution is stirred using magnetic stirrer about 7 hrs. The filtered solution is kept safely in a similar manner. Good quality single crystals of rhodamine doped BHT are collected from the solution during the time of 15 days. The photocopy of the grown crystals of pure and doped BHT are shown in Fig. 1.

Characteristic studies

Single-crystal X-ray Diffraction

The single crystals of doped BHT are subjected to X-ray diffraction studies using an Enraf Nonius Cad4 X-ray dif-

Corresponding Author:

R. Raja, Department of Physics, SCSVMV, Kanchipuram 631561, India;
Email: sridev_raja@yahoo.com

ISSN: 2231-2196 (Print)

ISSN: 0975-5241 (Online)

Received: 22.09.2018

Revised: 25.10.2018

Accepted: 22.11.2018

fractometer, using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) to determine the unit cell parameters. The lattice parameters of this measurement are listed in Table 1. These values agree well with the reported values of pure BHT and the grown crystal retains its original structure. This result reveals that, the Rhodamine B has entered into the lattice sites of BHT.

Fourier Transform Infra-Red Spectroscopy

The Fourier transform infrared spectrum of Rhodamine B doped Butylated Hydroxy Toluene was recorded at 300 K in the range of 4000–400 cm^{-1} using the KBr pellet technique. The Spectra of DBHT are shown in Fig 2 and the recorded FTIR assignments are tabulated in Table. 2. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data[10].

The Peak observed at 3407 cm^{-1} is mainly due to O-H stretching vibrations. The band appearing at 2920, 2851 cm^{-1} is mainly due to C-H stretching mode of vibration. Similarly the band appearing at 723 cm^{-1} are due to C-H out of plane deformations. Among the major peaks the intense absorption at 1625 cm^{-1} is attributed to C=O asymmetric stretching vibrations of COOH group. The peak at 1497 cm^{-1} is due to N-O asymmetric stretching and 1318 cm^{-1} is due to C-O stretching. The peaks at 1231 and 1113, 1157, 1060 cm^{-1} are due to C-H wagging and C-N stretching vibrations respectively. There is a change in percentage of organic elements due to the addition of dopant of Rhodamine B and the functional groups of the pure BHT crystal are identified by the FTIR spectrum at its positions as shown in the spectra.

UV-Visible spectral analysis

The UV-Vis. absorption spectrum of the doped BHT crystals are shown in Fig. 3. It is observed that BHT absorbance varies in the region 200-300 nm. There are no characteristic absorptions observed in the region between 300 and 800 nm which justify that the pure and doped BHT crystal are suitable for optical applications.

SHG Efficiency Studies

Kurtz and Perry technique is used to study the nonlinear optical efficiency of the doped BHT crystal [11,12]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, pulse width of 8 ns and with a repetition rate of 10 Hz was used. The grown single crystal of DBHT was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect the intensity of 532 nm component. The generation of the second harmonics was confirmed by the emission of green light. Hence the output power of the grown crystal was 8 mv for the input power of 5.7 mj/pulse, and the reference material (KDP crystal) having 10.8 mv. The SHG efficiency of the doped BHT crystal obtained is 0.8 times than that of KDP.

Thermal Analysis

The thermal studies of the crystal is one of the important studies for the suitability of fabrication of nonlinear optical devices. The thermal characterization of the grown single crystal DBHT was carried out by thermogravimetric (TG) and differential thermal analysis (DTA) studies using NETZSCH analyzer in the nitrogen atmosphere at the heating rate of 10 $^{\circ}\text{C}/\text{min}$ in the temperature range between from 25 to 500 $^{\circ}\text{C}$ and the resultant thermogram is shown in the Fig. 4.

The TGA curve shows that there is a loss of weight in the range between 75 $^{\circ}\text{C}$ - 175 $^{\circ}\text{C}$ in association with a sharp endothermic peak in DTA, which can be ascribed to the absorption of energy for breaking of bonds at the initial stage of decomposition. The TGA illustrates that there is no loss below 74.1 $^{\circ}\text{C}$, thus assigned as the melting point of the crystal. From the results of DTA, this is observed that no transformation inside the structure was observed before melting point of 74.1 $^{\circ}\text{C}$. The second endothermic peak at 172.7 $^{\circ}\text{C}$ and the percentage of weight loss of the crystal is 99%. The sharpness of this endothermic peak of doped BHT single crystal shows the good degree of crystallinity of the sample.

Dielectric Studies

The dielectric properties of doped BHT crystals were carried out in the frequency range 100–5MHz using an impedance analyzer HIOKI 3635model LCR meter. The dielectric constant and dielectric loss of doped BHT crystal as a function of frequency at different temperatures is shown in Fig. 5 and 6. The large value of dielectric constant at low frequency is due to the presence of space charge polarization [13]. The decrease in the values of ϵ_r with the frequency is due to the fact that the frequency of electric charge carriers cannot follow the alternation of the ac electric field applied beyond a certain critical frequency [14]. This exhibits the normal dielectric behavior of doped BHT single crystal. The dielectric graph endorses the independent behavior of dielectric constant at higher frequency for different temperatures. The lower value of ϵ_r and also its independent nature with respect to temperature at higher frequencies show the higher optical quality of the crystal. The magnitude of ϵ_r depends on the degree of polarization of charge displacement in the crystals. The dielectric constant of a material is due to the contribution of electronic, ionic, orientation and space charge polarizations, which depend on the frequencies[14].

The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) was calculated by using the relation

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad \tan \delta = \epsilon_r D$$

Where C is the capacitance, d 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 and D is the dissipation factor.

The dielectric loss of a material is mainly depends on the dissipation factor. A material must have low dissipation factor for use in device fabrications.

AC Conductivity studies

Figure 7 shows the variations in a.c conductivity of doped BHT crystal for different temperatures and different frequencies. The conductivity of doped BHT crystal increases with increasing temperature. The AC conductivity is calculated using the relation

$$\sigma = \omega \epsilon_0 \epsilon_r \tan \delta$$

where, ω is angular frequency of applied electric field. From the graph, it is observed that the AC conductivity increases with frequency of applied field suggested that the resistivity decreased with increasing the frequency. It indicates the dielectric breakdown frequency of the material.

Microhardness Studies

Microhardness measurements of DBHT single crystal were made using Shimadzu HMV-2 micro hardness tester fitted with a Vickers diamond pyramidal indenter. The grown crystal with smooth and dominant face was selected for microhardness studies. The indentation time was kept as 5s for all the loads. The Vickers hardness (Hv) was calculated from the relation [15].

$$H_v = 1.8544(P/d^2) \quad \text{Kg/mm}^2$$

Where, P is the applied load (measured in N) and d^2 is the area of the indentation (measured in meter square). The Vickers test is reliable for measuring the hardness of metals and also used for ceramic materials. The variations of microhardness of the doped crystal with the applied load is shown in fig.8.

Elastic stiffness and yield strength measurement

The details about tightness of bonding between neighbouring atoms is explained by elastic stiffness constant C11. The stiffness constant for different loads are calculated using Wooster's empirical formula [16], and the calculated values are tabulated. It is identified that the stiffness constant increases with the increase of load and are shown in Fig. 8 and 9. High value of C11 indicates that the binding forces between the ions are quite strong.

$$C_{11} = H_v^{\frac{7}{4}}$$

One of the important mechanical property of the grown crystals is yield strength σ_y for device fabrication[17]. It is a point at which material exceeds the elastic limit. Yield strength can be calculated by the relation (9) and the calculated values of yield strength of all crystals are presented in Table. 3.

$$H = 3\sigma_y$$

Meyer Index (n)

Variation of micro-hardness with applied load is usually explained for spherical indenter by Meyer's law and pyramidal indenter by Kick's law [18]. Later on Kick's law was modified by Hay and Kendall [19]. For pyramidal indenter Kick's law is given as,

$$P = kd^n$$

Where, P is the applied load in gram (or Newton), d is the observed diagonal length of indentation mark, and n is the constant for a given material. Onitsch pointed out that an n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials [20]. The n values observed in the present analysis suggesting that doped BHT crystals are soft materials.

CONCLUSION

The grown single crystal of rhodamine doped Butylated Hydroxy Toluene is grown by slow evaporation solution growth method. The crystal system of the doped crystal are orthorhombic and studied by the single crystal XRD analysis. The transparency nature and the suitability for optical applications is analyzed by UV-Vis. Spectral analysis. The second harmonic generation efficiency of the doped crystal is measured by Kurtz powder technique. The functional groups of the crystal are analyzed by FTIR spectral analysis. The TGA/DTA analysis is useful to study the thermal stability of the doped crystal. The measured mechanical strength of the crystal suggests that the crystal is a soft material.

REFERENCES

1. Zyss S J., Molecular Nonlinear Optics, Materials, Physics and Devices, Academic, New York, 1994.
2. Boyd. B.J., Nonlinear Optics, Academic, San Diego, CA, 1992.
3. Muthu K, Bhagavan Narayana G, and Meenakshi Sundaram S. P, "Growth, structure, crystalline perfection and characterization of Mg(II)-incorporated tris(thiourea)Zn(II) sulfate crystals: Enhanced second harmonic generation (SHG) efficiency", Jour. Alloys Com., 2013, Vol. 548, pp. 201-207.
4. Chithambaram V, Jerome Das S, and Krishnan S, "Synthesis, optical and dielectric studies on novel semi organic nonlinear optical crystal by solution growth technique", Jour. Alloy. Com., 2011, Vol. 509, pp. 4543- 4546.
5. Lakshamana Perumal C. K, Arulchakkaravarthi A, Rajesh N. P, Santhanaraghavan P, Huang Y. C, Ichimura M, and Ramasamy P, "Synthesis, crystal growth and FTIR, NMR, SHG studies of 4-methoxy benzaldehyde-N-methyl-4-stilbazolium tosylate (MBST)", Jour. Cryst. Growth, 2002, Vol. 240, pp. 212-217.
6. Uthrakumar R, Vesta C, Bhagavannarayana G, Robert R, and Jerome Das S, "Optical, crystalline perfection and mechanical

studies on unidirectional grown bis(thiourea) cadmium zinc chloride single crystal", Jour. Allo. Com., 2011, Vol. 509, pp. 2343-2347.

7. Rai R. N, Ramasamy P, and Lan C. W, "Synthesis and crystal growth of binary organic NLO material UNBA", Jour. Cryst. Growth, 2002, Vol. 235, pp. 499-504.
8. Raja R., Seshadri S., Saravanan R.R., "Crystal growth, spectral, thermal and optical properties of an organic single crystal – Dye doped hippuric acid" Optik ,2014,125, 916–919.
9. Raja R., Seshadri S., Gnanasambandan T., Saravanan R.R., Crystal Growth and Properties of NLO Optical Crystal –Butylated Hydroxy Toluene (BHT), Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,2014,
10. Chinna Babu P., Sundaraganesan N., Dereli O., Turkkan E., "FT-IR, FT-Raman spectra, density functional computations of the vibrational spectra and molecular geometry of butylated hydroxy toluene" Spectrochim. Acta Part A , 2011, 79, 562–569.
11. Kurtz S.K., Perry T.T., J. Appl. Phys., 39 ,1968, 3798.
12. Kurtz S.K., IEEE, J. Quantum Electron, 4, 1968, 578.
13. Mohd Anis, Hakeem D.A., Muley G.G., Optical and dielectric studies of KH_2PO_4 crystal influenced by organic ligand of citric acid and l-valine: A single crystal growth and comparative study , Results in Physics,2016, 6, 645-650.
14. Uma B., Sakthi Murugesan K., Jayavel R, Krishnan S., Milton Boaz B., Growth, spectral, optical, and dielectric studies on novel semiorganic NLO single crystal: d-phenylglycine hydrochloride, Applied Physics B, 2014, 115, 215-224.
15. Mott, B.W., Micro Indentation Hardness Testing, Butterworth, London, 1956.
16. Wooster, W.A., Physical properties and atomic arrangements in crystals, Rep. Progr. Phys., 1953, 16, 62-82.
17. Rani Christu Dhas, Benet Charles, J., Gnanam, F.D., Growth and microhardness studies on $\text{NH}_4\text{Sb}_3\text{F}_{10}$ single crystals, J. Cryst. Growth, 1994, 137, 295-298.
18. Sangwal K J Mater Sci 1989, 24, 1128.
19. Vineeta Gupta, Bamzai KK, Kotru PN and Wanklyn BM Mater Chem Phys 89 (2005). 64.
20. Onitsch, E.M., Micro-hardness Testing, Mikroskopie, 1950, 95, 12-14.

Figure 1: Grown crystal of pure and Rhodamine doped BHT.

Figure 2: FTIR spectrum of Doped BHT.

Figure 3: UV-Vis. spectrum of Doped BHT.

Figure 4: TGA/DTA analysis of Doped BHT.

Figure 5: Dielectric constant vs Log f.

Figure 6: Dielectric loss vs Log f.

Figure 7: Log f vs AC conductivity.

Figure 8: Load vs hardness of PDP crystal.

Figure 9: Log p vs log d of doped BHT crystal.

Table 1: XRD data and cell volume of pure and doped BHT crystals

Crystal	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)
Pure BHT	9.116	10.594	8.862	855.84679
Rhodamine doped BHT	9.15	10.65	8.92	868.9

Table 2: Assignments of Doped BHT

Wavenumber	ASSIGNMENTS
3407	O-H Stretch
2920, 2851	C-H stretch
1625	C=O asymmetric stretching
1497	N-O asymmetric stretch
1318	C-O stretch
1231	C-H wagging
1113, 1157, 1060	C-N stretch
723	C-H out of plane deformation

Table 3. Elastic stiffness and Yield strength of SP

Load (P) g	Hv (kg/mm ²)	C _n (x10 ⁻³ M Pa)	σ _y (M Pa)
25	53.5	10.379	174.891
50	62.9	13.778	205.62
100	73.15	17.944	239.127