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

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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

Analar 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.
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. 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 dielectric properties of doped BHT crystals were carried out in the frequency range 100–5MHz using an impedance analyzer HIOKI 3635 model 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 εr 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 εr and also its independent nature with respect to temperature at higher frequencies show the higher optical quality of the crystal. The magnitude of εr 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 (εr) and dielectric loss (tan δ) was calculated by using the relation

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \quad \tan \delta = \varepsilon_r \cdot \frac{d}{D}$$

Where C is the capacitance, d is thickness of the sample, $\varepsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$ 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.

**A C 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

\[
\sigma = \omega \varepsilon_0 \varepsilon \tan \delta
\]

where, \( \omega \) 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].

\[
Hv = 1.8544(P/d^2) \quad Kg/mm^2
\]

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.

\[
C11 = \frac{H_v^2}{P}
\]

One of the important mechanical property of the grown crystals is yield strength \( \sigma_y \) 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.

**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.

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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.

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**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.

| Crystal                  | a (Å)  | b (Å)  | c (Å)  | Cell volume (Å³) |
|--------------------------|--------|--------|--------|------------------|
| 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/mm²) | Cₚ (x10⁻² M Pa) | σ (M Pa) |
|------------|-------------|-----------------|----------|
| 25         | 53.5        | 10.379          | 174.891  |
| 50         | 62.9        | 13.778          | 205.62   |
| 100        | 73.15       | 17.944          | 239.127  |