Linear and Nonlinear Optical Studies on Novel NLO BaTr Single Crystal

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Abstract: ***Transparent single crystal of Barium L-Tartarate (BaTr) was grown by slow evaporation Technique. Single X-ray diffraction study was carried out for the grown crystal. The FT-IR studies confirm the presence of barium and tartaric acid in the grown crystal. The band gap energy of the BaTr crystal was calculated from the optical absorption spectrum. Theoretical calculations were made to determine the optical constants like absorption coefficient (α), extinction coefficient (K), Reflectance (R), refractive index (n), optical and electrical conductivity. Kurtz-Perry powder technique was carried out and the material is found to be exhibit nonlinear optical (NLO) property.***

Key words: BaTr, Organometallic, Non aromatic, Reflectance, Optical conductivity, Laser Damage

1. Introduction

The importance of the nonlinear optical interaction imposes severe demand on potential nonlinear applications. Extensive studies have been made on the growth of the nonlinear optical materials over the past few decades because of their potential applications in the field of telecommunication and optical signaling processing [1,2]. Semi organic nonlinear optical crystals have imposed a new approach in the field of second harmonic generation. They have combined properties of both organic and inorganic crystals like high damage threshold, wide transparency range, and high nonlinear coefficiency which make them suitable for fabrication of devices [3].

Organometallic compounds contain metal and organic ligands linked by coordination bond. These types of complexes are much interest in the field of optical fabrication. Organometallic complexes exhibit high mechanical strength and laser damage threshold strength compare to the organic and inorganic materials because they have metal ions in their crystal lattice.

The structure of the organometallic compound can be varied by changing the metal, co-ordination number and ligands [4]. Compounds of tartaric acid have variety of practical application in science and technology [5]. Tartaric acid crystals are used for nonlinear optical devices based on their optical second harmonic generation and optical transmission characteristics [6-8]. A number of tartaric acid based NLO complexes are reported earlier [9-11]. Crystal structure of Barium L-Tartarate was reported by C. Gonzalez-silgo et al. [12].

In the present work, non-aromatic organic tartaric acid and inorganic barium chloride are mixed to get organometallic barium L-Tartarate single crystal. Due to the proton ionization, the hydrogen atom in tartaric acid is easily removed and its replaced by Ba^{2+} ions to form the Barium L-Tartarate single crystal. Single crystal X-ray was carried out and cell parameters of the grown crystal were calculated. FT-IR studies were carried out and functional groups present in the crystal are analyzed. Measuring the optical constant is important for optical devices and fabrication. Systematic work was made to find the optical constants of the grown crystal. NLO property of the crystal was confirmed by Second Harmonic Generation Test.

2. Materials and Methods

2.1 Experimental

Highly pure Barium chloride salt and L-Tartaric Acid were taken in 1:1 equimolar ratio to synthesis Barium L-Tartarate single crystal. The calculated amounts of reactants were thoroughly dissolved in deionized water at room temperature. The resulting solution was filtered using a filter paper and allowed to evaporate at room temperature. Seed crystals were formed in 3 days from the prepared saturated solution. Seed crystals were collected carefully from the solution and recrystalized to grow bulk and transparent single crystal. Colorless single crystal of dimension 1.2×1.3×0.3 cm^3 was harvested in a period of 22 days. Figure 6.1 shows the photograph of as grown Barium L-Tartarate single crystal.

Figure 1: Photograph of as grown BaTr crystal

3. Results and Discussion

3.1 XRD analysis

Single crystal X-ray diffraction studies of BaTr crystal was carried out using an Enraf Nonius CAD-4/MACH 3 diffractometer, with MoKα radiation. XRD studies reveals that the lattice parameter values of the grown crystal are a = 8.129 Å, b = 9.107 Å and c = 8.426 Å and its crystallized in orthorhombic crystal system with the space group $P2_12_12_1$

.These values are in well agreement with those values reported by Gonzalez-silgo et al [12]. The cell parameter values of the grown BaTr crystal and the reported values [12] and is shown in Table 1.

Table 1: Lattice Parameter Values of BaTr crystal

Cell Parameters	Present work	Reported Values
A	8.129 Å	8.181 Å
B	9.107 Å	9.036 Å
C	8.426 Å	8.3920 Å
Crystal system	Orthorhombic	Orthorhombic
Volume	623.2442 $Å^3$	620.3661 $Å^3$
α=β=γ	90°	90°
Space group	$P2_12_12_1$	$P2_12_12_1$

3.2 FT-IR Studies

The FT-IR spectrum recorded of BaTr crystal is shown in the Figure 2. The spectrum is recorded in the region 400 cm^{-1} to 4000 cm^{-1} by using "LITAO3 MIR" spectrophotometer.

The OH stretching vibrations of the grown crystal produces a peak at 3857 cm^{-1}. The peak at 2360 cm^{-1} in the spectrum is due to C-H stretching vibration. The characteristic peak at 2187 cm^{-1} confirms the organometallic (Ba^{2+}) presence in the crystal system. The less intensity peaks absorbed between 2000 cm^{-1} - 2900 cm^{-1} are due to hydrogen bonding interaction of the Tartaric acid with the Barium ions.

The peak at 1598 cm^{-1} is due to the COO- symmetric stretching vibration. The absorption peaks in the region 400 cm^{-1} – 600 cm^{-1} assigned to the vibration of the modifier cations with respect to Barium atoms [13]. The peak at 702 cm^{-1} confirms the presence of Barium ions in the crystal [14].

3.3 Optical studies

3.3.1 Optical Absorption study

The transparency of the crystal plays an important role in the field of optical fabrication and optical signal processing [15, 16]. The good transparency of the crystal in the entire visible region suggests its suitability for SHG efficiency applications [17, 18]. The optical absorption spectrum of the BaTr single crystal was recorded in the wavelength region from 190 nm to 1100 nm and is shown in Figure 3.

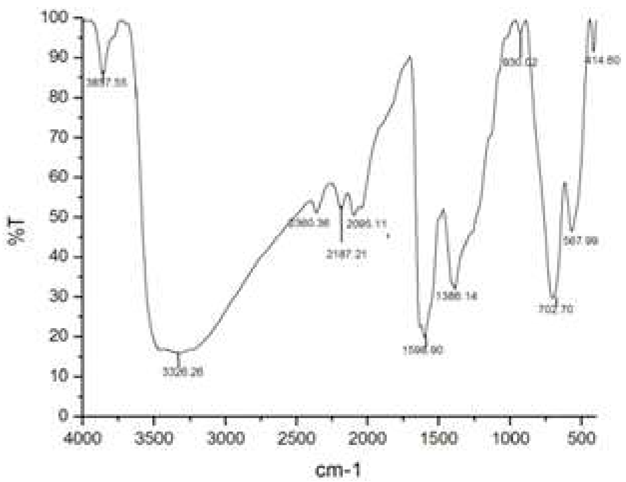

Figure 2: FT-IR Spectrum of BaTr crystal

From the graph it is evident that the lower cut off wavelength of the grown crystal is 237 nm and the crystal has wide transparency window between 200 nm – 1100 nm.

3.3.2 Determination of the optical constants

The optical absorption coefficient (α) of the crystal was calculated using the formula

$$\alpha = \frac{1}{t} \log 1/T$$

Where, t is the thickness of the crystal and T is the transmittance of the crystal. The optical band gap energy of the crystal can be from Tauc's plot. The extrapolation of the linear part [19] of the Tauc's plot shown in Figure 4, shows that the optical band gap energy of the BaTr crystal is 2.67 eV.

The extinction coefficient (K) to be obtained from the equation

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

Where, λ is the wavelength of the ultraviolet radiation .Figure 5 shows the variation of extinction coefficient (K) with the photon energy. The reflectance in terms of absorption coefficient can be written as

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

The variation of reflectance as a function of absorption coefficient is shown in Figure 6. From Figure 5 and Figure 6 it is clear that the extinction coefficient (K) and reflectance depend on the absorption coefficient. The internal efficiency of the material is also depending on the absorption co efficient [20].
The refractive index of the crystal can be calculated from the reflectance value and the equation

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

Where R is the reflectance and n is the refractive index. The refractive index of the material is found to be 1.46 at a wavelength of 1100 nm. The reflection coefficient (r) measures the fractional amplitude of the reflected electromagnetic field and it calculated from the square root of the reflectance value (R)

$$r = \sqrt{R}$$

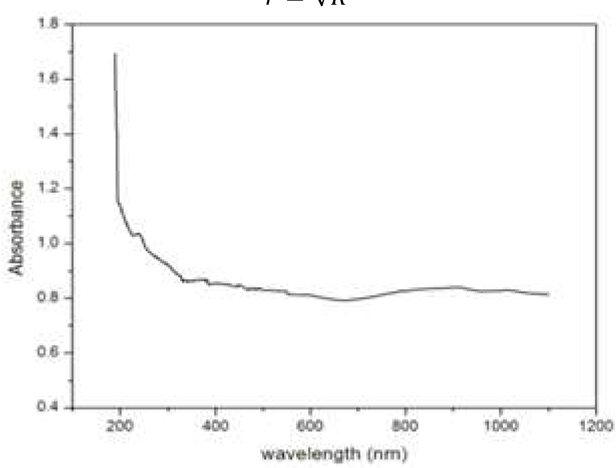

Figure 3: UV-Absorption Spectrum of BaTr crystal

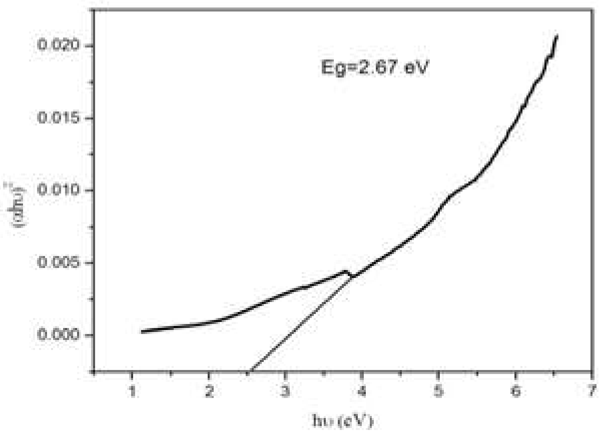

Figure 4: Tauc Plot of BaTr crystal ($(\alpha h\nu)^2$ vs Photon energy (hν)

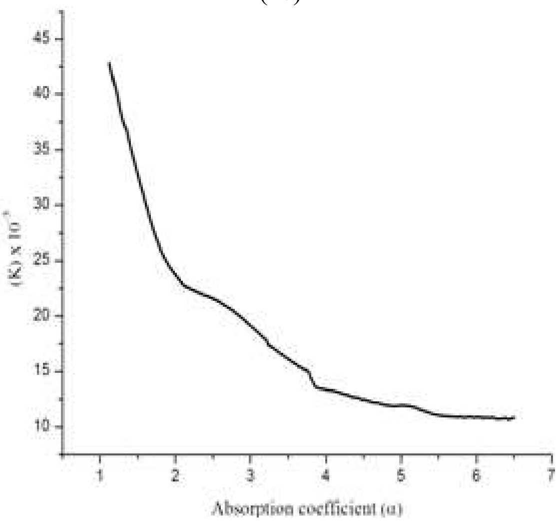

Figure 5: Plot of extinction coefficient

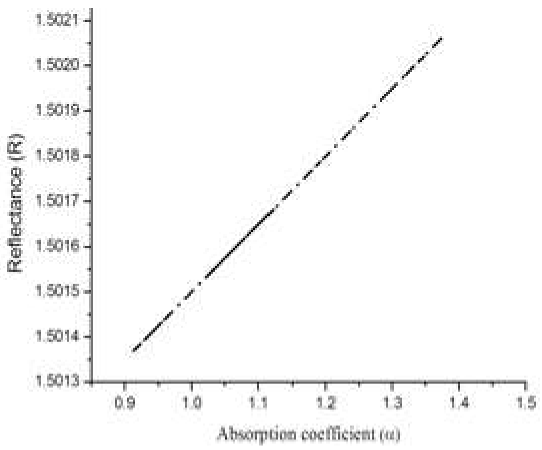

Figure 6: Plot of absorption coefficient (a) vs. reflectance (R)

Figure 7 shows the variation of reflection coefficient with photon energy. From the plot it is observed that the reflection coefficient first increases with increase in photon energy and reaches a maximum value at the photon energy 1.9 eV and then decrease gradually with increasing photon energy. This shows that the BaTr crystal reflects all the electromagnetic radiation at 1.9 eV.

3.3.3 Optical Conductivity

The optical conductivity (σ) of the crystal is mainly based on the optical parameters such as optical absorbance, reflectance and absorption coefficient. Good optical conductivity is the basic property for the fabrication of LED and Optoelectronic devices [21]. Optical conductivity is given by the relation

$$\sigma = \frac{\alpha n c}{4\pi}$$

Where c is the velocity of light, n is refractive index of the crystal. The optical conductivity of the crystal in the photon energy range 1 eV to 7 eV shows 4 distinct peaks at the photon energies 1.3, 3.2, 5.3 and 7 eV as shown in Figure 8.

These four peaks indicate regions of deeper penetration of electromagnetic waves and high conductivity. It was observed that the optical conductivity increases up to photon energy of 3.3 eV exhibiting the peak value of 1.82×10^{10}. Increase in optical conductivity up to 3.3 eV can be attributed to increase in absorption coefficient.
There is a reduction of the optical conductivity in the region of 3.3 eV to 3.9 eV, and it is due to decrease in absorption coefficient, after that the optical conductivity increases with photon energy. This indicates that this is the region of deeper penetration for electromagnetic waves and also it shows that the material has high optical conductivity.

The positive value of the optical conductivity is because of the decrease in extinction coefficient and it implies that there is an addition of conductivity of the grown crystal [22]. Thus the BaTr crystal can be optimized for high positive conductivity.

3.5 Second Harmonic Efficiency

The second harmonic nonlinear optical property of the as grown BaTr crystal was examined through the Kurtz-Perry powder technique [23]. The standard KDP crystal has been used as the reference material for the grown crystal. In this method powdered sample of randomly oriented crystallite particles were placed in between two glass slides. The sample was then subjected to the output of Q-switched Nd:YAG laser emitting a wavelength of 1064 nm with power of 5 mJ/pulse. It is observed that a signal of wavelength 532 nm was produced by the BaTr crystal. This reduction of wavelength implies the second harmonic frequency generation of the crystal. The output SHG signal of 29.7 mV for the BaTr crystal was obtained. The KDP crystal gave an output of 15.3 mV for the same input signal. Thus it is evident that the SHG efficiency of the grown BaTr crystal is 1.94 times that the KDP crystal and the crystal is suitable for device fabrication.

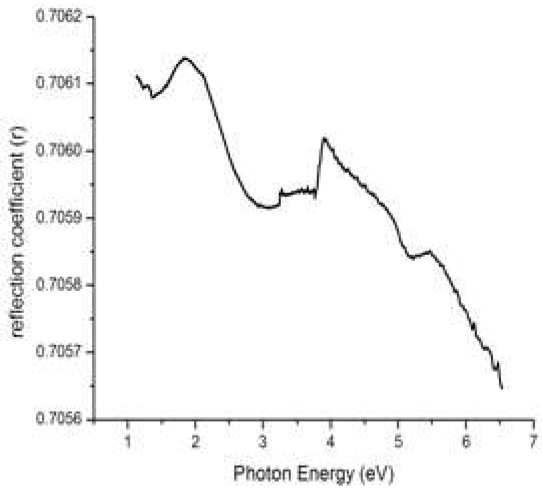

Figure 7: Plot of reflection coefficient (r)

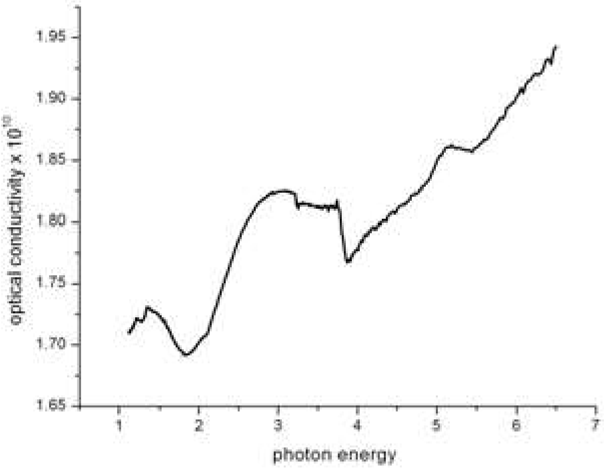

Figure 8: Plot of Optical Conductivity

4. Conclusion

Single crystal of Barium L-Tartarate was successfully grown by slow evaporation technique. Single X-ray diffraction study confirms the lattice parameter values of the grown crystal and it is in good agreement with the reported values. From the single crystal X-ray diffraction study the lattice parameter values of the crystal were found to be a= 8.129 Å, b= 9.107 Å and c= 8.426 Å and it is crystallized in orthorhombic crystal system with the space group $P2_12_12_1$. FT-IR studies confirm the presence of barium and Tartarate ions in the crystal. Optical studies were carried out for the grown crystal and the crystal has wide transparency window between 200 nm – 1100 nm. Various optical constants were calculated and the optical band gap energy of the crystal is found to be 3.17 eV. The extinction coefficient (K) and reflectance depend on the photon energy and absorption coefficient. The internal efficiency of the material is also depends on the absorption coefficient. The BaTr crystal reflects all the electromagnetic radiation that falls in at 1.9 eV. The refractive index of the material is found to be 1.46 at a wavelength of 1100 nm. Optical conductivity is calculated from the UV - Vis absorbance value and the grown crystal possesses high optical conductivity. The SHG efficiency of the grown BaTr crystal is 1.94 times of that the KDP crystal and the BaTr crystal is suitable for device fabrication.

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