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Studies on Single Crystal Growth, FT-IR Spectral, Optical, SEM, EDAX and Thermal Analysis of Benzyl Triphenylphosphonium Chloride Monohydrate

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ABSTRACT

Good quality single crystals of Benzyl Triphenylphosphonium Chloride Monohydrate (BTPC) were successfully grown using a slow evaporation solution method with water as the solvent at room temperature. The crystal structure was determined to be monoclinic system with space group P21/c. The lattice parameters obtained are a = 9.85 Å, b = 19.99 Å, c = 11.59 Å, $\alpha = \gamma = 90°$ and $\beta = 109.75°$ as revealed by single crystal X-ray diffraction. Fourier Transform Infrared (FT-IR) analysis confirmed the presence of various functional groups in the material. UV-visible absorption analysis indicated a lower cut-off wavelength at 296 nm and an optical bandgap of 4.2 eV, suggesting potential for photonic applications due to the broad transmission in the visible region. Scanning Electron Microscopy (SEM) and Elemental analysis (EDAX) were utilized to confirm the surface morphology and constituent elements present in the material. Thermal analysis (TG-DTA) revealed that the material is stable up to 339°C, which corresponds to its melting point.

Keywords: Single crystal Growth, X-ray diffraction, FT-IR, Optical studies, SEM, TG-DTA

Introduction

An uncontrollable increase in optoelectronics and photonics paves the way for materials with excellent nonlinear optical (NLO) properties. Nonlinear optical materials are important in applications such as optoelectronic switching, frequency conversion, and limiting strong light [1]. They can interact with a material that can generate new frequencies or affect the characteristics of the inputted lights. Organic second- and third-order NLO materials, as well as organometallic compounds, have been widely researched due to the high nonlinear optical response they possess [2], ease of production, and possibility of tuning by chemical modification.

Recent developments in the synthesis and characterization of organ phosphonium materials have focused attention on their NLO applications [3]. The insertion of phosphorus in the molecular structure enhances both the nonlinear response and lengthens thermal/chemical resistance. Inherent to the BTPM is a chemical constitution that fosters efficient NLO through its primary

structure [4]; phosphonium groups and benzyl rings used in conjunction with hydrate create an exceptional energetic niche. The molecular structure of the title compound is shown in Figure 1.
In the present investigations, single crystal of Benzyl Triphenylphosphonium Chloride Monohydrate was grown by slow evaporation solution growth technique using water solvent at ambient temperature. Further it was characterized by single crystal x-ray diffraction, Fourier transform infrared (FT-IR), UV-Visible analysis, Scanning electron microscopy along with elemental analysis (EDAX) and thermal studies (TG-DTA).

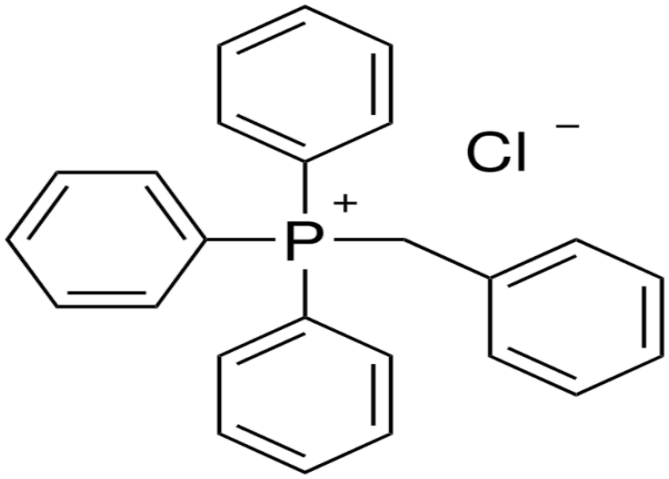

Figure 1 Molecular structure of BTPC

2. Materials and Methods

2.1 Growth of BTPC Single Crystals

The single crystals of BTPC were obtained using low temperature solution method using water as solvent. The commercially available material was dissolved in a aqueous solution and stirred well using motorized stirrer for about 5 hours to get the homogeneity. The crystal growth rate is influenced by its solubility and the temperature [5]. Once saturation was achieved, the equilibrium concentration of the solute was analyzed gravimetrically [6]. Then the homogeneous solution was carefully filtered using Whatman filter paper and housed in a constant temperature bath. After a span of 15 days, good quality single crystals were harvested from the mother solution is shown in Figure 2.

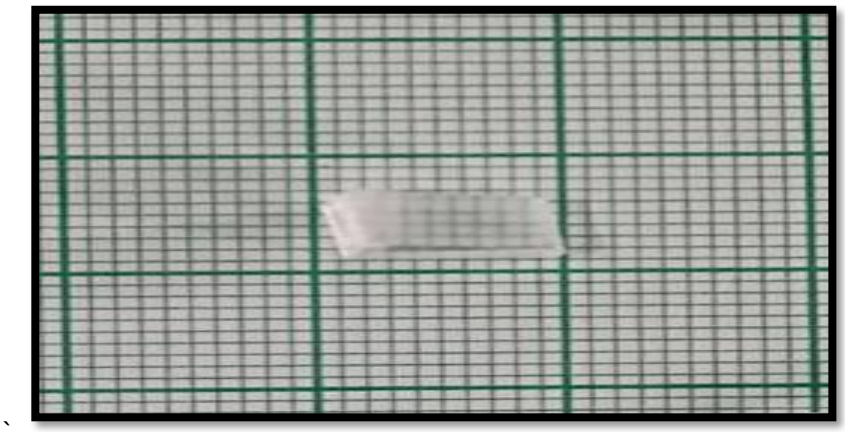

Figure 2 As grown single crystal of BTPC

3. Results and Analysis

3.1 Single crystal X-ray diffraction analysis

The as grown single crystal of BTPC was subjected to single crystal X-ray diffraction analysis of the title crystal using a BRUKER KAPPA X-ray diffractometer with Mokα (λ = 0.71072Å) radiation at room temperature. The study confirmed that the title compound crystallizes in a monoclinic system with space group P21/c. The lattice parameters obtained are a = 9.85 Å, b = 19.99 Å, c = 11.59 Å; $\alpha = \gamma = 90°$, $\beta = 109.75°$ were consistent with previously reported values [7].

3.2 Fourier Transform infrared (FT-IR) Analysis:

The FT-IR spectrum of the title compound was recorded in the range of 400 to 4000 cm^{-1} using a Bruker AXS FT-IR spectrophotometer, as shown in Figure 3. The FT-IR spectrum provides valuable insights into the functional groups present in the material. The intense band detected at 3315 cm^{-1} is attributed to O-H stretching vibrations, which indicates that the water molecules are included in the hydrate framework. The peaks at 3052 and 2856 cm^{-1} are assigned to aromatic C-H stretching vibrations in nature, while the peaks of IR data presented as 1576 and 1485 cm^{-1} are bisexually allocated for assignment signals attributable to C=C stretching vibrations. The 1433 and 1318 cm^{-1} peaks indicate the presence of C-H bending vibrations. The sharp peaks at 1165 cm and 1033 cm^{-1} are assigned to P-O-C stretching vibration, which indicates that the phosphonium group was present. Peaks less than 1000 cm^{-1} indicate complex skeletal vibrations, such as C-P, C-Cl, and other vibrational modes.

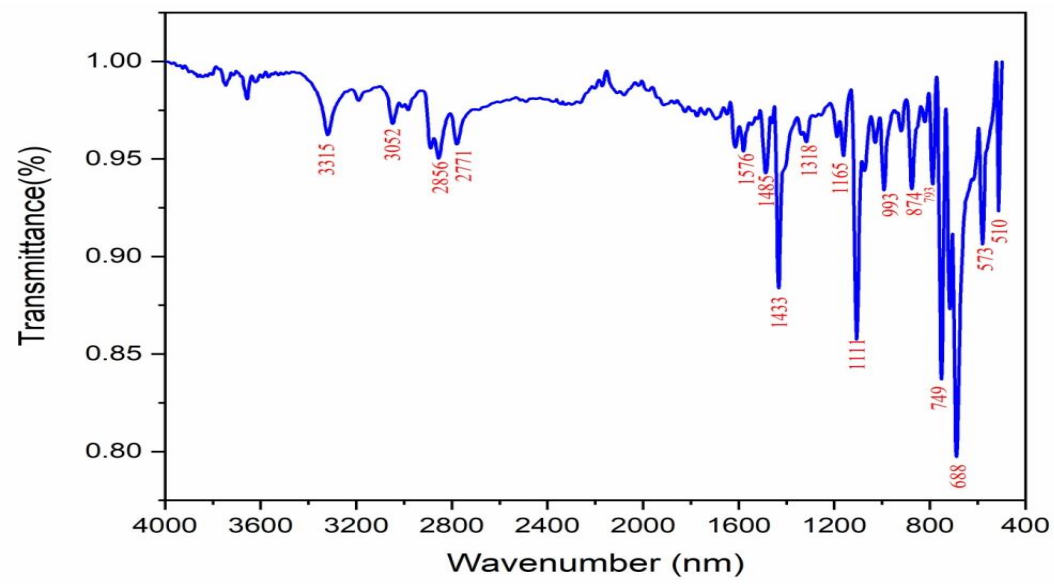

Figure 3. FT-IR spectrum of BTPC

3.3 UV-Visible Analysis:

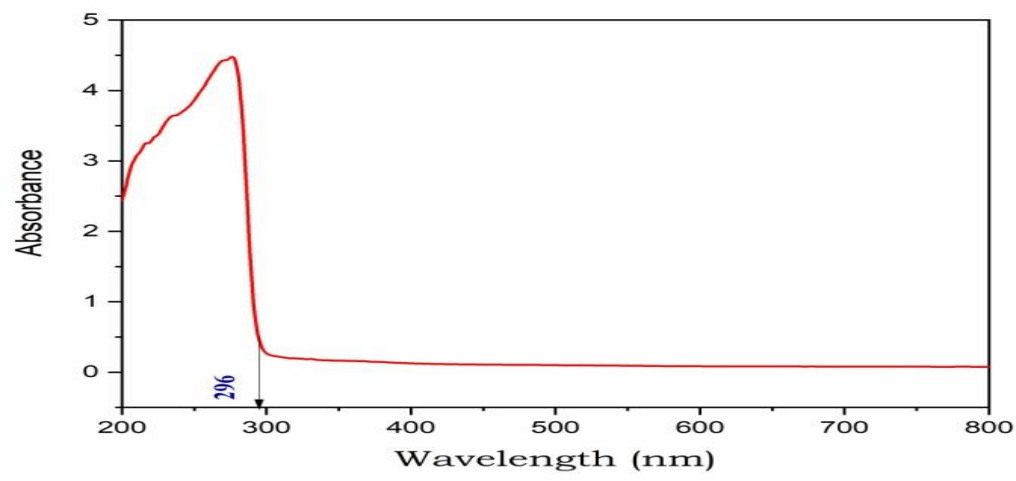

Figure 4. UV-Visible absorbance spectrum of BTPC

The UV-visible spectrum provides insights into the molecule's structure, as the absorption of UV and visible light involves the promotion of the electron from the ground state to higher states. The optical studies were carried out using a Perkin-Elmer Lambda-35 UV-visible spectrophotometer, covering the 200 – 800 nm wavelength range. Figure 4 and 5 shows the UV-Visible absorbance and transmittance spectrum of the title compound. Lower cut-off was observed at 296 nm and the grown crystal demonstrated good transmittance (Figure 5) throughout the visible region, making it suitable for NLO applications [8].

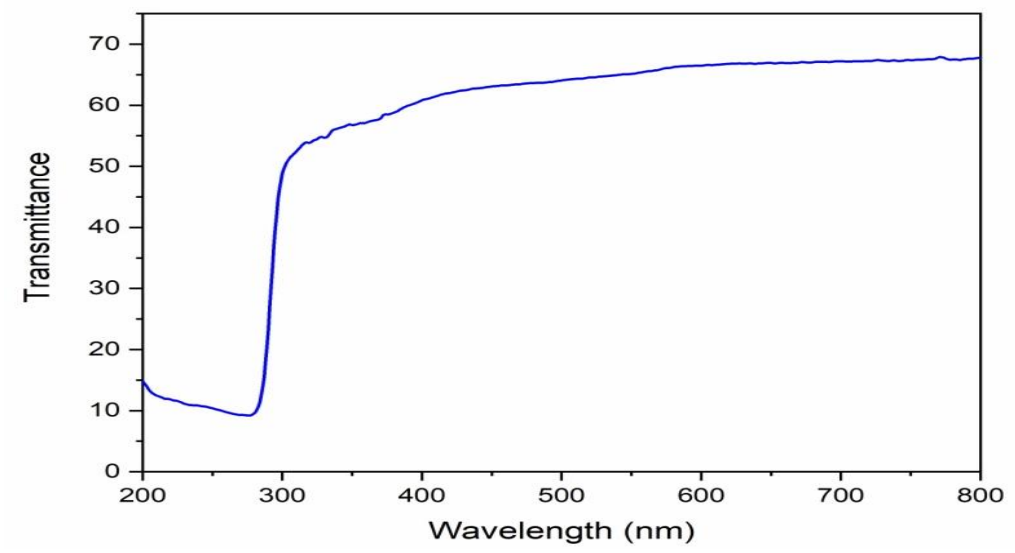

Figure 5. UV-Visible transmittance spectrum of BTPC

The UV-Visible absorbance data was used to calculate the optical band gap, which is shown in Figure 6. The plot of energy (hυ) versus $(\alpha h\upsilon)^2$, where "α" represents the absorption coefficient, helped determine the optical band gap energy, which was found to be 4.2 eV by extrapolating the slope region where it intersects the x-axis. The wide bandgap affirms the crystal's high transmittance in the visible region, making it well-suited for optoelectronic applications [9].

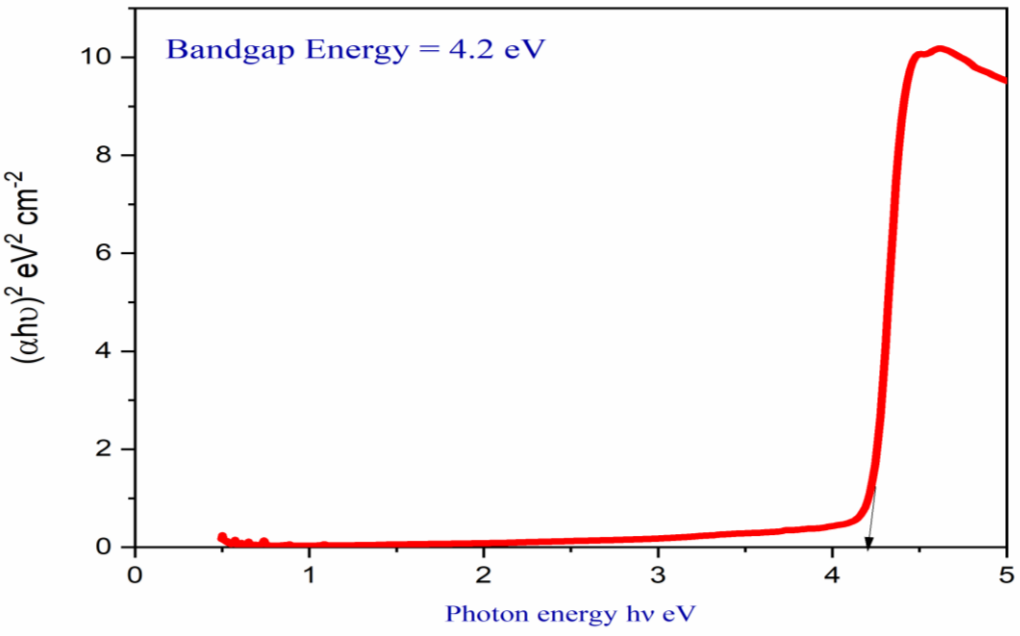

Figure 6. Variation of Photon energy (hν) with$(\alpha h\nu)^2$

3.4 SEM with EDAX Analysis:

The surface morphology of BTPC crystal was studied using Quanta 200 FSEM instrument with different magnifications and the respective images are shown in Figure 7. SEM images indicate a smooth and intact surface with minimal irregularities with spherical in nature. EDAX analysis to identify the elemental composition of single crystal BTPM was carried out which is shown in Figure 8. The spectrum further confirmed the chemical composition of the compound, as it contained C, P, and Cl signals. The elemental compositions present in the spectrum were carbon (81.56%), phosphorus (9.02%), and chlorine (9.42%). Here, the relative ones correspond directly to element abundances.

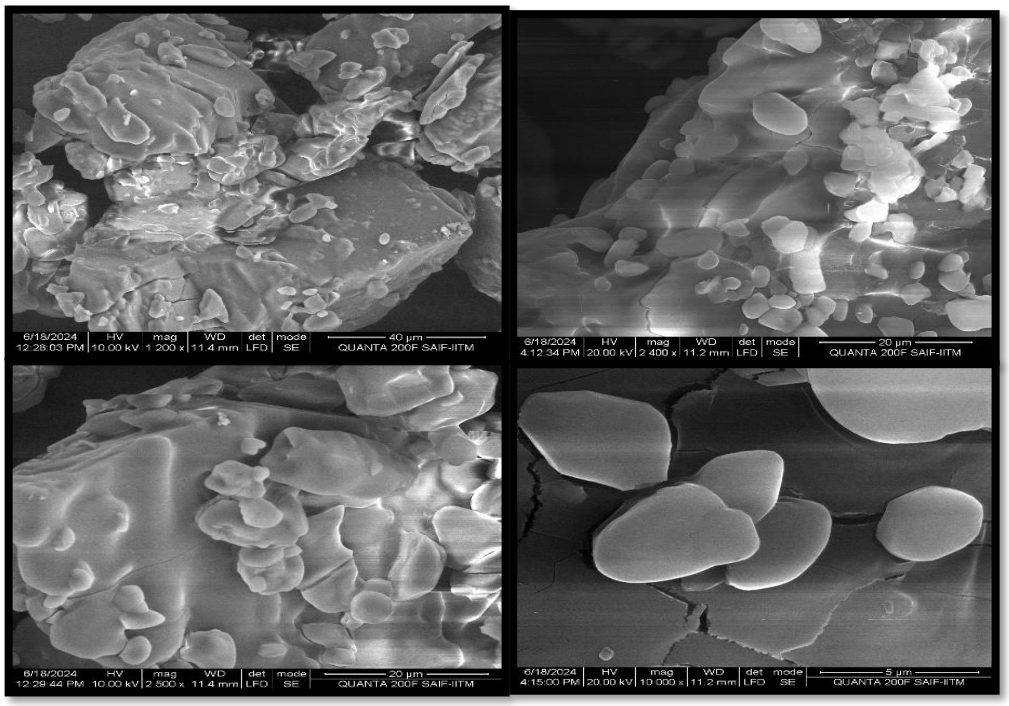

Figure 7. SEM Images of BTPC crystal with different magnifications

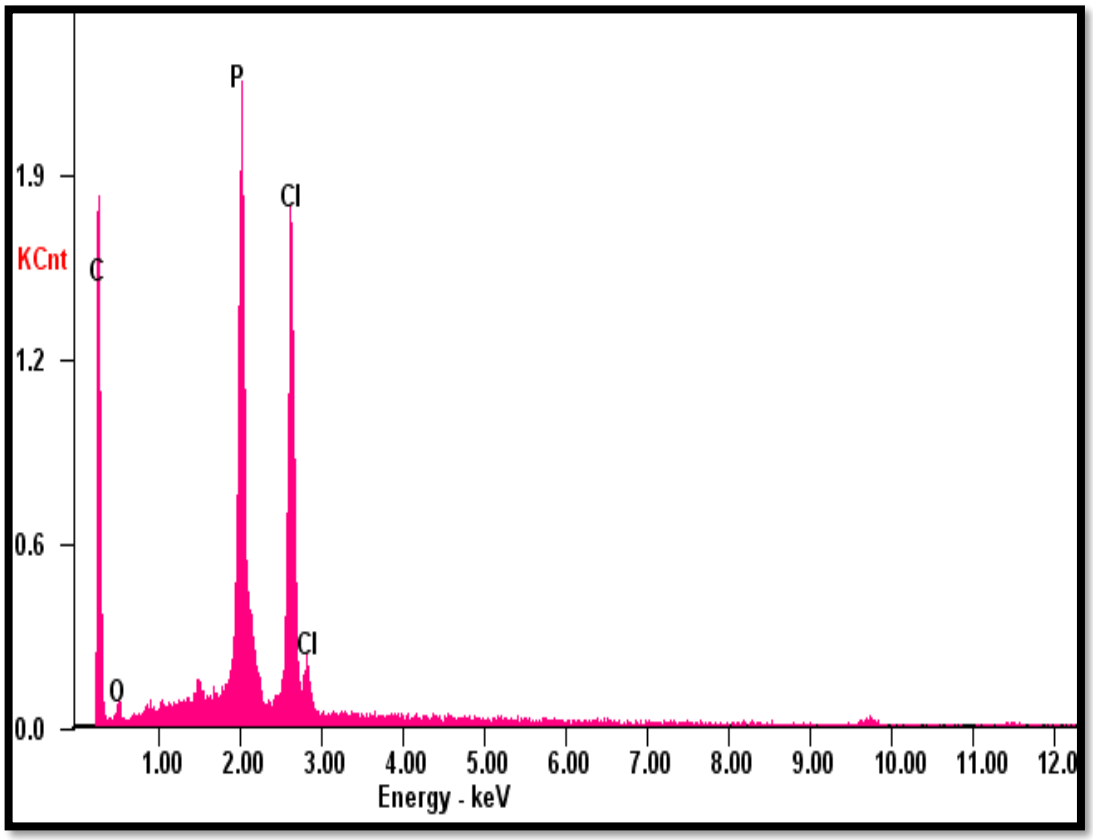

Figure 8. EDAX spectrum of BTPC

3.5 Thermal (TG-DTA) Analysis:

The thermogravimetric and differential thermal analysis of the title material were conducted in a nitrogen atmosphere at a heating rate was set at 10 k/min, and the study was performed using the NETZSCH STA 409C thermal analyzer. According to the TG-DTA curve, the results revealed a two-stage breakdown. Figure 9 shows the TG-DTA curve of BTPC crystal. The decomposition begins only at 350 °C, and there is also a substantial weight loss. The DTA curve provides information on the thermal transitions, thus adding to that provided by TG data.

An endothermic peak at 339°C, coinciding with the weight loss on the TG curve, implied that there was an endothermic degradation of material. The sharp endothermic peak shows the good degree of crystallinity of the sample [10] The absence of peaks indicates a lack of large phase transitions or melting events within the temperature range investigated. From the graph, there is a sharp endothermic peak at 339°C which is assigned to be the melting point of the material.

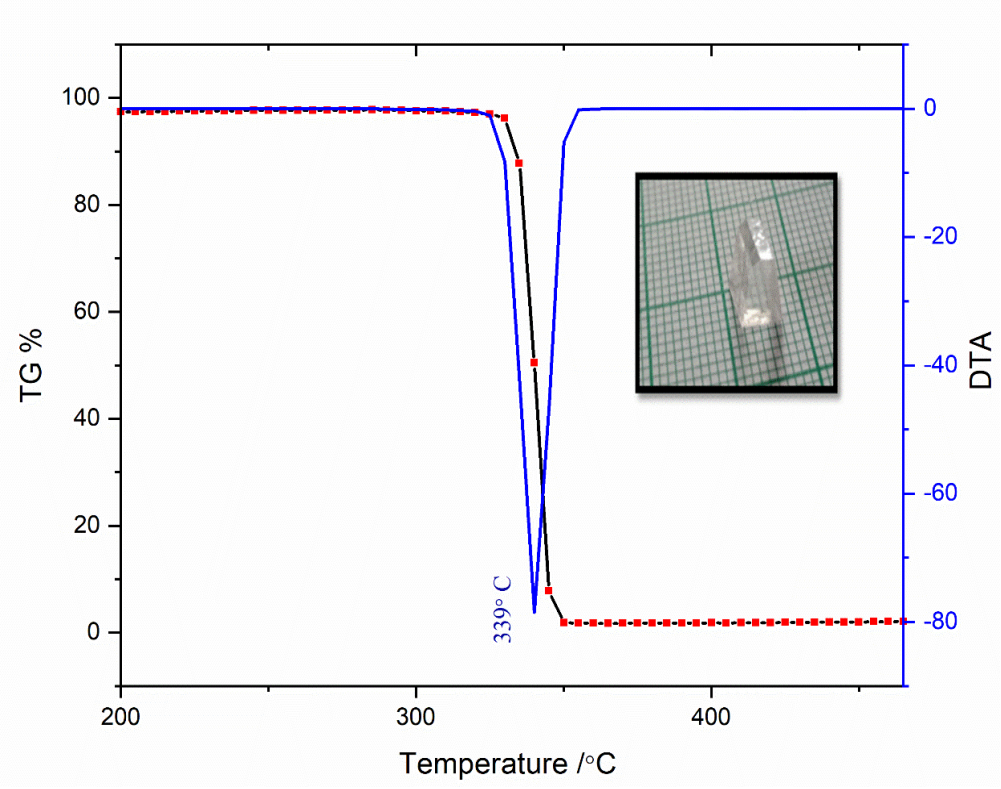

Figure 9. TG DTA curve of BTPC

A comparative Table 1 shows the potential like materials were compared with Benzyl Triphenylphosphonium Chloride Monohydrate and their research findings were tabulated. Table 1 gives the significant research findings of BTPM with other phosphonium-based materials [11-13].

Table 1. Comparative analysis of BTPC with other NLO crystals

References	Material	Crystal System	Key Findings
Present Study	BTPC	Monoclinic	High transparency, potential for NLO applications
[11]	Benzyl Phosphonium Bromide	Orthorhombic	High third-order NLO efficiency, strong third harmonic generation (THG)
[12]	Triphenylphosphonium Chloride	Triclinic	Significant UV absorption, moderate NLO properties
[13]	Benzyl Phosphonium Fluoride	Monoclinic	Enhanced photoluminescence, good third-order NLO response

4. CONCLUSION

Good quality nonlinear optical single crystal of Benzyl Triphenylphosphonium Chloride Monohydrate was grown using the slow evaporation solution growth technique at room temperature for the first time. The study confirmed that the title compound crystallizes in a monoclinic system with space group P21/c. and the obtained lattice parameters are a = 9.85 Å, b = 19.99 Å, c = 11.59 Å; $\alpha = \gamma = 90°$, $\beta = 109.75°$ were consistent with reported literature. The various functional groups present in the material were identified via FT-IR spectral analysis. The optical properties were examined, revealing a lower cut-off wavelength of 296 nm and an optical band gap was observed at

4.2 eV. Surface morphology and elemental analysis were confirmed by SEM and EDAX analyses. The thermal stability was tested using TG-DTA and it is stable up to 339°C.

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