Synthesis, growth, structure, spectroscopic, and physicochemical properties of 18-Crown-6-ether barium (II) bisthiocyanate monohydrate single crystal: BCBT

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Abstract: We reported the bulk size with a dimension of 18×5×5 mm³ single-crystals of 18C6(Ba)(SCN)₂H₂O [18-crown-6-ether barium(II) bisthiocyanate monohydrate]; abbreviated as BCBT, have been grown from an aqueous solution via slow evaporation solvent technique(SEST). The grown pristine single-crystals have characterized by single crystal X-ray diffraction (XRD), FT-IR, micro-Raman, and UV-Vis-NIR spectral studies. BCBT crystallizes in a monoclinic with a non-centrosymmetric space group of P2₁ crystal system. Additionally, the chemical etching studies showed that the reverse crystal growth rates of BCBT. The FT-IR studies confirmed the present of functional groups in the grown single-crystal of BCBT. Interestingly, the CN stretching observed at 2012 cm⁻¹ is clearly shown the N-bonded nature of SCN with Ba²⁺. Moreover, the micro-Raman spectrum is used to further additional confirmation of BCBT single-crystal. In the entire visible region, the BCBT crystal has found to be wide (UV-Vis-IR) optically absorption from 231 to 800 nm, which is suitable for optoelectronic applications. The laser damage threshold measurements on the BCBT crystal with Q-switched Nd: YAG laser of fundamental wavelength 1064 nm (QUANTA RAY Model LAB – 170 - 10, pulse width 10 ns and repetition rate 6 Hz used as the source of light for laser damage threshold experiment. Moreover, the thermal stability of grown BCBT is stable up to 289 °C. From the results reveal that the sample possess admirable thermal stability compared to other IOPS series such as CLTC (171°C), and ACCTC (241°C).

1. Introduction

Nowadays, the organometallic based crystalline compounds have been searched for the ability of nonlinearity, and applications have high performance in photonic device fabrications. Recently, the inorganic nonlinear optical materials have not able to fulfil the present obligation; the need for novel properties has turned the consideration of the material researchers towards the organometallic compounds, which combine the merits of the inorganic and organic materials. A major reward of organometallic compounds leads to charge transfer into the metal to ligand [M-L], or ligand to metal [L-M]. It is provides large polarizations and raises the nonlinear optical (NLO) efficiency. The broad ranges of central metal atoms are joining with various ligands of different sizes, oxidation states, and
nature provides the structural flexibility to modify properties up to a maximum [4, 5]. The greater NLO efficiency, excellent physico-chemical properties, and good chromophore have thiocyanate based organometallic single crystals. Recently the researcher and scientist are focused on the inorganic polymer with organic sphere (IOPS) based (SCN) ligand. The ligand ion is a suitable chromophore for second-order NLO properties, and it forms coordination compounds with metal ions such as Zn$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, and Hg$^{2+}$. The metal complexes formed with a noncentrosymmetric space group, high thermal stability, and favorable environmental security can attract applications cutting across various fields [6-9]. Hence, based on the above factors, attempts were made to combine the organic ligand thiocyanate with metal ions (Zn and Ba) to improve the NLO, higher harmonic generations, and other properties. Thiocyanate (SCN)$^-$ based transition metal compounds of second and third-order harmonic generation materials have numerous advantages, which make them potential materials for crystal growth engineering. In the present work, we have synthesized and grown a non-centrosymmetric BCBT crystal, which has barium as the central metal atom and thiocyanate as the chromophore. Earlier, the structure of the BCBT reported [10]. Since it crystallizes under a non-centrosymmetric P$2_1$ crystal system, the same factor has motivated us to explore its structure, spectral, linear and nonlinear optical properties. Herein, the single crystal XRD and the characterization such as FT-IR, micro-Raman, UV-Vis-absorption, chemical etching, laser-damage threshold (LDT) and thermal stability (TG-DTA, DSC) of compound BCBT has analyzed systematically and reported.

2. Experimental method

A mixture of molar ratio 1:2:1 comprising of 18-crown-6(C$_{12}$H$_{24}$O$_6$), potassium thiocyanate (KSCN) and barium chloride monohydrate (BaCl$_2$.H$_2$O) have dissolved in the aqueous solution and continuously stirred for three hours so as to get a homogeneous mixture. All the chemicals used for following reactions are with analytical reagent grade. This mixture has poured into a clean glass beaker and filtered homogeneous clear solution is covered by transparent polyethylene sheet, and it contains a fine pin holes on it. Finally, the filtered solution has allowed slowing evaporation solvent technique (SEST). The photograph of the as grown crystals with dimension of 18×5×5 mm$^3$ is depicted in figure 1.

$$C_{12}H_{24}O_6 + BaCl_2.H_2O + 2KSCN \rightarrow C_{14}H_{26}BaN_2O_7S_2 + 2KCl$$

Figure 1. Bulk single crystals of BCBT
3. Results and discussions

3.1 Single crystal X-ray diffraction studies

The grown BCBT single-crystal X-ray diffraction (S-XRD) pattern and lattice parameters have been measured by Bruker Kappa (APEX II CCD) graphic monochromatic radiation (Mo-Kα radiation, (λ=0.71073 Å) at 293 K. From the S-XRD result shows that it belongs to a non-centrosymmetric monoclinic crystal system with the space group of P2₁ and cell parameter a = 7.9868(4) Å, b = 17.2739(9) Å and c = 8.5242(5) Å, Volume V=1100.74 (10) Å³ and Z=2. The important parameters of BCBT crystal has listed in table 1 and the observed values are compared with the results obtained from earlier reported [10]. In this structure, the barium atom has 9-fold coordination coupled with two nitrogen and 7-oxygen atoms. Figure 2 is depicted the 30% probability displacement ellipsoids in the molecular structure of BCBT. The Ba-O bond lengths are 2.803 Å to 2.852 Å respectively. All the oxygen atoms, except water molecule, which is coordinating with barium atom, are lying in the same plane. But the carbon atoms associated with the oxygen atom are not in the plane. There are two types of hydrogen bonds such as C-H...S and O-H...S are observed with the donor hydrogen distance which varies between 0.84 Å to 0.97 Å and hydrogen acceptor distance in the range of 2.54 Å to 2.92 Å and also the distance between donor to acceptor distance changes from 3.294 Å to 3.787Å. O-H...S hydrogen bond leads to the formation of an infinite 2-D network of the structure (figure 3). The 3-D structure is formed by the stacking of this long chain. It is evident by the presence of neither hydrogen bond nor short contact between two layers.

![Figure 2. 30% probability displacement ellipsoids and the atom-numbering scheme of BCBT single-crystal](image1)

![Figure 3. O-H...S hydrogen bond leads to the formation of an infinite two-dimensional network of the structure BCBT](image2)
3.2 Chemical Etching studies

The physical properties such as optical, electrical, dielectric and hardness have been affected by the presence of an impurity, nature of the materials, pH, temperature, solvent, and missing of atoms in lattice site, etc. The chemical etching is one of the most useful to understand the reverse growth rate and any defect present in the crystal surfaces. In order to understand a reverse growth rate of single-crystal by using chemical etching analysis [11]. Here the water is an etchant. The title compound BCBT has immersed in double deionized water for an etching time of 10s and 20s. Further, the immersed BCBT crystal has taken out and dried with the electric drier and instantaneously positioned at an optical microscope. The optical microscope showed the layered pattern for the etching periods of 10s and 20s. Figure 4 depicts the layered itching patterns, which are shown in 2-D mechanisms.

![Figure 4. a) Before etching b). After etching 10s and c). After etching 30s](image)

3.3 IR and FT-Raman Spectral analysis

The FTIR spectra of BCBT were recorded in KBr medium in the range of (4000–400) cm\(^{-1}\) and is shown in figure 5a. In the higher frequency range, the strong and sharp peak at 3412 cm\(^{-1}\) denotes the occurrence of OH stretching. It is known that CN stretching vibrations often lies higher than 2000 cm\(^{-1}\), SCN bending lies around 860 cm\(^{-1}\). In the present case, CN stretching mode of vibration is observed at 2012 cm\(^{-1}\) and SCN bending is observed at 835 cm\(^{-1}\). The strong peak at 2919 cm\(^{-1}\) and the shoulder peak at 2830 cm\(^{-1}\) are assigned to CH\(_2\) asymmetric and symmetric stretching respectively.

The sharp peak at 1625 cm\(^{-1}\) is due to the bending of water molecule which is coordinated with Ba. The peaks at 1090 cm\(^{-1}\) and 540 cm\(^{-1}\) are assigned to the bending vibrations of SCN. The peaks at 1286 cm\(^{-1}\) and 1246 cm\(^{-1}\) may be due to CH\(_2\) bending. The peaks at the lower frequency at 1452 cm\(^{-1}\) and 1350 cm\(^{-1}\) are assigned to CN stretching. The observation of CN stretching at the lower frequencies may be due to the coordination of the SCN with barium atom. The twin weak peaks at 1272 cm\(^{-1}\) and 1244 cm\(^{-1}\) corresponding to CH\(_2\) bending. The Raman shift at the lower range of 287 cm\(^{-1}\), 129 cm\(^{-1}\),

Table 1. Single crystal data of BCBT

| Empirical formula | C\(_{14}\)H\(_{26}\)Ba N\(_2\)O\(_7\)S\(_2\) |
|-------------------|----------------------------------|
| Molecular weight  | 535.83                           |
| Temperature       | 293(2) K                         |
| Wavelength        | 0.71073 Å                        |
| Crystal system    | Monoclinic (α = 90°,β = 110° and γ = 90°) |
| Space group       | P2\(_1\)                          |
| Unit cell dimensions | a = 7.9868(4) Å | b = 17.2739(9) Å | c = 8.5242(5) Å |
| Volume            | 1100.74(10) Å\(^3\)             |
| Z                 | 2                                |
and 88 cm\(^{-1}\) may be due to the presence of BaO group. The existence and binding of S-C-N ligand have strongly influenced and the strong peak observed at 2015 cm\(^{-1}\) as shown in figure 5b.

![FT-IR spectrum of BCBT](image)

**Figure 5a. FT-IR spectrum of BCBT**

![FT-Raman spectrum of BCBT](image)

**Figure 5b. FT-Raman spectrum of BCBT**

### 3.4 Optical absorption studies

The ultraviolet (UV) optical absorption is an important role in nonlinear optical properties of both second and third-order harmonic generations respectively. UV-Vis spectrometer (SHIMADZU, UV 3600 PLUS) has used to measure optical absorption of grown single-crystal of BCBT in the range of 200 to 800 nm. The results showed the cut-off wavelength of BCBT single-crystal is 231 nm. If any crystalline materials have less than 270 nm, those materials may be exits good transparency, and nonlinear optical properties are second and third harmonic generation. Furthermore, the title compound of BCBT has a very less absorption value of ultraviolet to infrared (UV-IR; \~270nm to 800nm) and through the entire visible region. It is noteworthy, the UV optical absorption results reveal that the grown title compound of BCBT cut-off wavelength (231 nm) (Figure 6) is better than the other organometallic SCN\(^-\) family crystals like MFCTC (330nm) and ACCT (241 nm) [12-13].

![UV absorbance spectrum of BCBT](image)

**Figure 6. UV absorbance spectrum of BCBT**
3.5 Laser damage threshold (LDT) measurement

To measure the laser damage threshold (LDT) of BCBT single-crystal by using a Q-switched Nd: YAG (Quanta-Ray-Model LAB-170-10 pulse-width 10 ns and repetition rate 6 Hz.) doped insulator laser with a fundamental wavelength of 1064 nm. The title compound of BCBT single-crystal with dimensions of (5×5×2 mm³) has placed on the sample holder, and it is focused on a converging lens with a 200 mm focal length. The grown single-crystal of BCBT crystal plane (110) has subjected to sample-holder, and the laser beam focused on the BCBT crystal plane (110). The incident beam intensity has increased in a step by step until the crystal surface gets damaged. A damaged BCBT crystal plane (110) has observed by the eye and noted the damaging input energy. In the present study, the crystal has damaged by increasing the input energy about 159 mJ and the observed value of laser damage threshold has found to be 2.35 GW/cm².

3.6 Thermal stability studies

The thermal stability of BCBT crystalline material has measured by SDTQ 600V-20.9, thermal analyzer and heating rate of 10 K/min under nitrogen (N₂) are shown in figure 7a and figure 7b. The different decomposition states of grown single-crystal BCBT measured by thermo-gravimetric (TG) with various temperatures has confirmed by a differential scanning calorimetric analyzer (DSC). The traced TG–DTA graph proved that the grown single crystal of BCBT is stable up to 289 °C and the sample of BCBT undergoes into three different decomposition stages.

The first state of decomposition occurs by the presence of water molecules in BCBT single crystal. In the second stage of decomposition in the TG curve in the breakdown of BCBT in two compounds such as 18-Crown-6-ether (18C6) and Ba(SCN)₂ may take place successively in the second stage. The calculated experimental value of 30.45 % nearly coincides with the total theoretical value of 35.25%. Finally, all the left-over molecules get liberated simultaneously before 1000 °C without any residues. From the result reveals that the title compound of BCBT have excellent thermal stability with compared to other IOPS series of metal thiocyanate family crystalline materials such as CLTC (171 °C), KCCTC (241 °C) and organometallic family crystalline materials such as MCCTC (181 °C), and AMCTC (151 °C) [14-17].

4. Conclusion

The synthesized title compound of BCBT crystal structure has confirmed by S-XRD pattern and it belongs to a non-centrosymmetric monoclinic system with a space group of P2₁. The UV-Visible, FT-IR, and micro-Raman spectroscopic studies have carried out to investigate the optical cut-off wavelength, functional groups, and various vibrational modes of the grown crystal of BCBT. The
second harmonic efficiency measurement of BCBT single-crystal does not show any second harmonic generation efficiency. It may be due to the absence of π electrons and very few hydrogen bonds. Hence, the title compound is may be promoted to higher (third) harmonic generations.

The thermal stability of grown single BCBT is thermally stable up to 289 °C confirmed and verified by TG-DTA and DSC thermal analyzers. The laser damage threshold measurement value of BCBT single-crystal is found to be 2.35 GW/cm². The reverse growth rate of BCBT single-crystal has confirmed towards chemical etching analysis, which indicated the layered pattern for etching periods of 10s and 20s. Based on the above results shows it is a potential material of photonic device fabrications such as phase matching, optical mixing, and optical switching devices.

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