Synthesis, Growth and Characterization Aspects of Non-linear Organometallic Single Crystals of BCTZ

K.Showrilu[1], V.Naga Lakshmi[2], K.Rajarajan[3, a]

1 – Research and Development Centre, Bharathiar University, Coimbatore-641046, Tamil Nadu, India

2 – Ch.S.D.St.Theresa's autonomous College for women,Eluru,West Godawari-534003, Andhra Pradesh, Tamil Nadu, India

3 – Department of physics, Rajeswari Vedachalam Government Arts College, Chengalpattu-603001, Tamilnadu, India

a – drkrr2007@gmail.com

DOI **10.2412/mmse.82.69.288** provided by Seo4U.link

Keywords: solution growth, orthorhombic system, HPLC.

ABSTRACT. Bis[(18-Crown-6)Potassium][Tetrakis(isothiocyanato)Zinc(II)],[$(18C_6)K]_2$ [$Zn(SCN)_4$] (BCTZ), a novel organo-metallic crystal, was grown from ethanol-water mixed solvent by a slow evaporation solvent technique which were found to be crystallized in a non centrosymmetric space group p_{na21} of an orthorhombic system. The spectroscopic, optical, mechanical properties of [$(18C_6)K]_2$ [$Zn(SCN)_4$]; BCTZ were investigated by FT-IR, FT-Raman, UV-Vis-NIR techniques. The hardness of the grown crystal of BCTZ was measured by Vickers hardness measurement tester. The purity of the crystalline compound was verified by HPLC studies. The UV-Vis study reveals that the title compound was optically transparent in the visible region, which is suitable for non-linear optical applications.

Introduction. The application of single crystals in the newest technology is evident from the recent developments in semiconductors, polarizers, transdures and infrared detectors etc. The organo-metallic thiocyanate complexes are appropriate for recognizing blue-violet light by frequency doubling of laser radiation. The experiments conducted by the eminent scientists all over the world strongly favour the possible use of this class of materials for various non-linear optical applications and photonics device fabrications [1]. It is fascinating to note that the metal thiocyanate complex family crystalline compounds suggest a mixture of molecular structures in turn these complexes are capable of efficient frequency conversion of IR radiation to ultraviolet wavelength. In meta thiocyanate complexes, the thiocyanate has the capability to interconnect metal ions with its own donors S and N [2-4].

Previously, Zhang and Zelmon [5] have reported the growth of a new NLO crystal [$(18C_6)K$] [$Cd(SCN)_3$]; KCCTC, which is transparent from 220 to 3300 nm and shows second harmonic generation (SHG). Recently, Zhang and Shou [6] and Zhang and Huang [7] have reported the growth and characterization aspects and powder SHG of [(18C6)Li] [$Cd(SCN)_3$]; CLTC, respectively. The thermal and optical properties of ACCTC [(NH_4)] [$Cd(NCS)_3$].$C_{12}H_{24}O_6$ was reported by V. Ramesh and K. Rajarajan [8].

In the present work, a nonlinear optical crystalline compound Bis [(18-Crown-6)Potassium] [Tetrakis (isothiocyanato) Zinc (II)]; [$18C_6(K)]_2$[$Zn(SCN)_4$]; BCTZ has been synthesized and single crystals of 5x4x3 mm^3 were obtained. The structural details of BCTZ were already reported by A.N.Chekhlov [9]. However, the characterization aspects of BCTZ were not reported elsewhere. Hence, in the present case, efforts were made to synthesize and grow the good quality single crystals and thereby the spectral, optical, thermal and mechanical studies were carried out on the sample and reported for the first time.

Experimental procedure. The required amount of starting materials of AR grade (purity>98.0%) were purchased and were utilized to grow the single crystals of BCTZ. To synthesize the title compound, 18-Crown-6, potassium thiocynate and Zinc Chloride were taken in the molar ratio 2:4:1 and dissolved in ethanol-water mixed solution (volume ratio 3:1) and stirred thoroughly for three hours to obtain a homogeneous solution and was filtered with WHATMAN 110 µm filter paper. The filtered solution was left to facilitate evaporation. Colorless single crystals of BCTZ were obtained within a week.

Characterization. Single crystal X-ray diffraction (SXRD) analysis was carried out on BCTZ using Bruker Kappa APEX11CCD diffractrometer with graphite monochromated M_o-K_α radiation (λ=0.71073Å) to determine the lattice parameters. BRUKER IFS 66 V FT-IR spectrometer used to analyze the various functional groups of element. FT-Raman spectrum was recorded in the range 400-4000 cm^{-1} using BRUKEF RFS 27 Raman Spectrometer to know the different types of vibration modes. The TG-DSC analysis of BCTZ was done using SDT Q 600 V20.9 thermal analyzer in the temperature range 30-1000 °C at the rate of 10 K/min. The microhardness measurement of well polished BCTZ crystal of dimension 5x4x3 mm^3 was carried out by a REICHERT MD 4000 E ultra microhardness tester with a diamond indentor. The sample was further subjected to high performance liquid chromatography study using HPLC instrument to determine the purity of the grown crystal.

Results and discussion

Single crystal XRD. BCTZ crystal belongs to the in a non-centrosymmetric orthorhombic system with Pna21 space group. The lattice parameters obtained are a=17.604(4) Å, b=14.190(3) Å, c=17.625(6) Å, V=4403(2) Å, Z=4. The compound consists of one $[Zn(NCS)_4]^{2-}$ anion and two host-guest $[K(18\text{-crown-}6)]^+$ cations [9], all coupled through one bridging anionic SCN^- ligand into a tri nuclear complex molecule $[K(18\text{-crown-}6)]_2[Zn(NCS)_4]$ (Fig. 1)

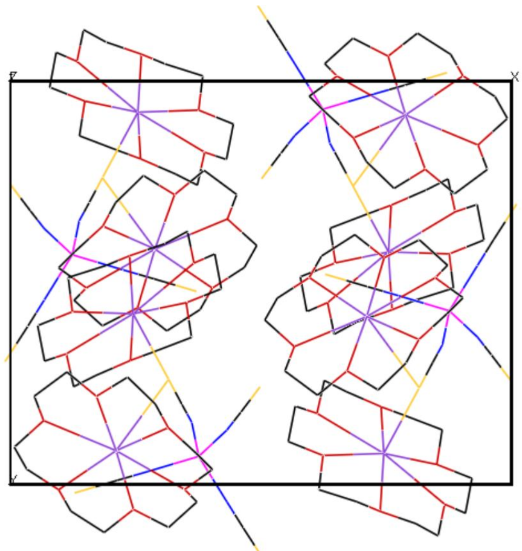

Fig. 1. Crystal packing of BCTZ along ‘c’ direction.

FI-IR analysis. The powdered sample of BCTZ was subjected FT-IR studies to confirm the occurrence of functional groups and coordination of ligands in the wave number range 400-4000 cm^{-1}. The middle IR spectrum of BCTZ is shown in Fig. 2. The present investigation confirms that the CN stretching mode of KSCN appears as a strong and very sharp bond at 2113.98 and 2073.48 cm^{-1}, which indicates that the thiocyanate group is coordinated to the metal ions through nitrogen.

Similarly, the SCN coordination is evident from the SCN bending observed at 478.58 cm^{-1}. Thus, in the BCTZ sample, the N-bonded nature has been confirmed by FT-IR analysis. The sharp peak bands observed at 1103.28 and 960.55 cm^{-1} were shifted from 1037 and 940 cm^{-1} of pure 18-Crown-6 respectively, which is due to symmetric and asymmetric C-O-C stretching vibrations. In addition, the sharp and intense band observed at 1350.17 was shifted from 1333 cm^{-1} of BCTZ [11], which is due to $–CH_2$- stretching vibration. The selected FT-IR spectral assignments of BCTZ listed in Table 1.

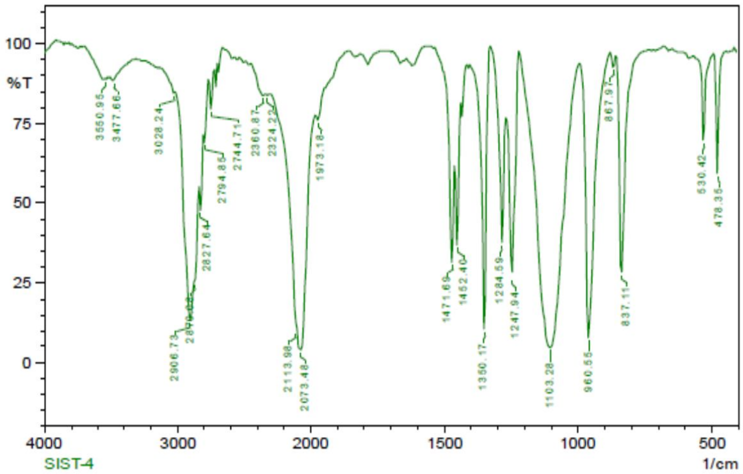

Fig. 2. FT-IR spectrum of BCTZ.

Table 1. Selected FT-IR spectral assignments of BCTZ.

Wavenumber (cm^{-1})	Assignments
478 , 530	NCS symmetric bending vibrations
837	Twice NCS bending vibrations
867	Twice NCS bending vibrations
960	Symmetric C-O-C stretching vibrations
1103	Asymmetric C-O-C stretching vibrations
1452	CH_2 Stretching vibrations
1471	CH_2 Stretching vibrations
2073	CN stretching vibrations
2113	CN stretching vibrations
2970	NH stretching vibrations

FT-Raman studies. The Raman spectrum obviously shows the vibration modes at 279.09 and 245.53cm^{-1} respectively, which confirm the coordination of Zn ions with the SCN ligand. In addition, the presence and binding of the SCN is observed as a strong peak observed at 2112.51cm^{-1} that corresponds to the stretching vibration of CN. From the structure point of view, it is evident that the Zn atoms are tetrahedrally coordinated with four nitrogen atoms (Fig 2).

Thermal analysis. The TG-DSC analysis of BCTZ was performed using SDT Q 600 V20.9 thermal analyzer in the temperature range 30-1000 ^{0}C at 10 K/min. The TG curve of BCTZ shows the decomposition of the sample at various temperatures (Fig 3). In the grown crystal, there is no weight loss up to 100^0C, indicating absence of water in the molecular structure BCTZ and the DSC profile shows that the thermally stability of the sample is 210.7 ^{0}C.

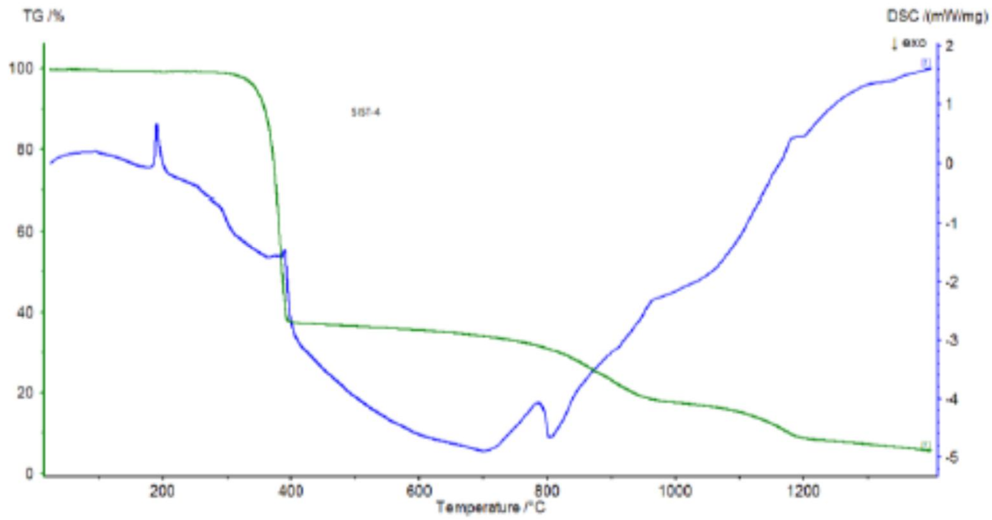

Fig. 3. TG-DSC profile of BCTZ.

Vickers's Micro hardness. Hardness is the one of the very important physical properties, which can be used as a suitable measure to analyze the strength of the material. The microhardness measurement was carried out on the well-polished BCTZ crystal of dimension 5x4x3 mm^3 using REICHERT MD 4000 E ultra micro hardness tester with a diamond indentor. The Vicker's hardness values of BCTZ were estimated for different applied loads. A graph is drawn with the parameters hardness (H_v) and load (p) as shown in Fig 4. It is clear from the graph that the hardness number increases with increasing load up to 100 g. Hardness attains saturation above 100g, which may be due to the outcome of internal stresses generated locally due to indentation

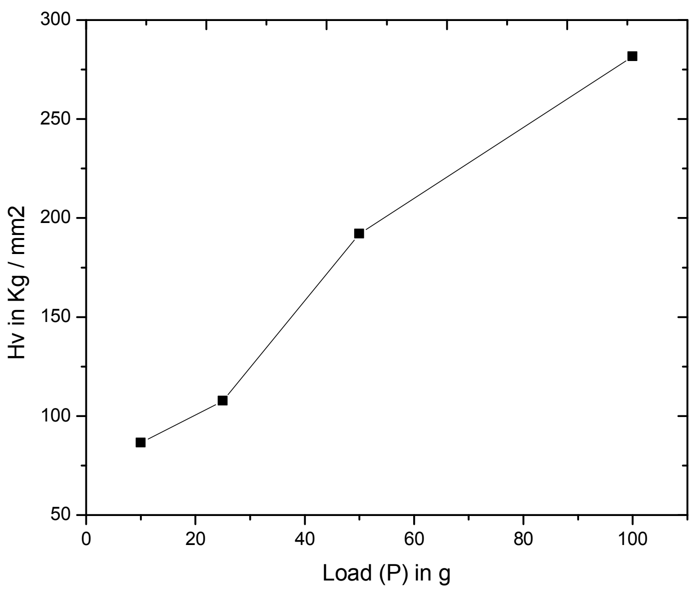

Fig. 4. Hardness Vs Load profile of BCTZ.

HPLC Studies. To realize the purity of the crystalline materials of BCTZ, the sample was subjected to High performance liquid chromatography study using HPLC instrument. The spectrum shows single peak with the retention time of 3.969 minutes with the peak voltage of 490 mv. The peak with high resolution clearly shows that BCTZ sample is pure.

UV–Vis spectroscopy. The UV-Vis spectra of BCTZ in ethanol-water aqueous solution (volume ratio 3:1) were recorded with 200 - 800 nm wavelength bands. From the spectral profile (Fig 5), it is evident that BCTZ optically good in the visible region including part of IR and UV. The wavelength minimum is found to be 226.4 nm. The absence of absorption in the above mentioned region reveals the suitability of the sample for NLO applications.

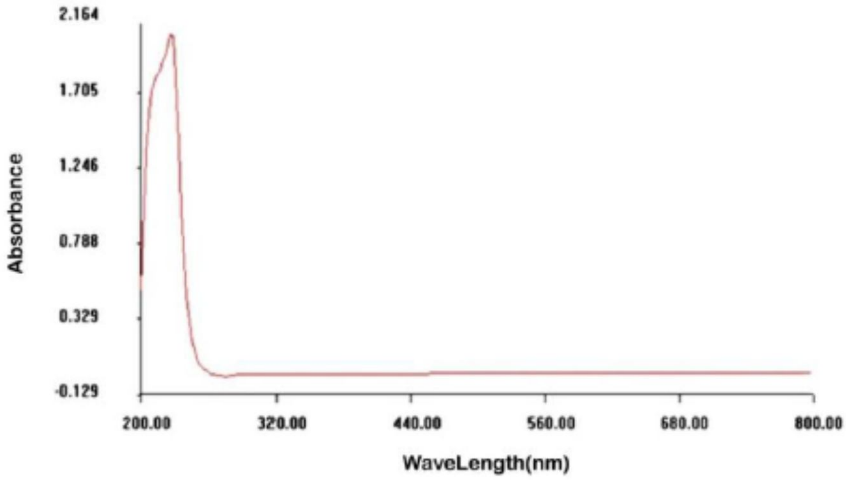

Fig. 5. UV-Vis- Absorbance spectrum of BCTZ.

Summary. Optically transparent and good quality crystals of BCTZ were grown successfully by slow evaporation method. The crystal structure was analyzed using standard crystallographic procedures. The UV cut-off wavelength is observed to be 226 nm, which is suitable for producing blue-violet light using diode laser. The functional elements of BCTZ were analyzed through FT-IR and FT Raman studies. The low absorption in the visible region shows that these crystals are usable in SHG. Thermal studies reveal that the BCTZ sample stable up to 210.7 ^{0}C. The mechanical properties were analyzed. The purity of the compound was confirmed by HPLC technique. From all these studies, it can be concluded that the title compound BCTZ is a potential material for NLO applications.

Acknowledgements. One of the authors K. Rajarajan extends sincere thanks & gratitude to University Grants Commission (UGC) and Tamil Nadu State Council for Higher Education (TANSCHE) for funding the research project. The authors acknowledge the Sophisticated Analytical Instrument Facility (SAIF), IIT-Madras and VIT, Vellore for the facilities extended towards characterization.

References

[1] K. Rajarajan, S. Selva kumar, Ginson P.Joseph, I.Vetha Pother, M.Gulam Mohamed, P. Sagayaraj J., Crst.Growth 286 (2006) 470 DOI: :10.1016/j.jcrysgro.2005.10.092.

[2] I. Vetha Potheher, K. Rajarajan, M. Vimalan, S. Tamilselvan, R. Jeyasekaran, P. Sagayaraj, Phys. B 406, (2011) 3210 DOI:10.1016/j.physb.2011.05.025.

[3] A. Gacemi, D. Benbertal, B.B. Muriel, A. Lecchi, A. Mosset, Z. Anorg. Allg. Chem. 629, (2003) 2516 DOI: 10.1002/zaac.200300243.

[4] X.T. Liu, X.Q. Wang, X.J. Lin, G.H. Sun, G.H. Zhang, D. Xu, Appl. Phys. A 107(2012) 949 DOI: 10.1007/s00339-012-6829-2.

[5] H. Zhang, D.E. Zelmon, J. Cryst. Growth 234 (2002) 529.

[6] J.J. Zhang, X. Shou, Spect. Chimi. Acta Part A Mole. Biomole.Spect. 74 (2009) 532.

[7] J.J. Zhang, Y. Huang, Powder second harmonic generation measurement and thermal decomposition mechanisms of a new organometallic compound [(18C6)Li][Cd(SCN)3], Cryst. Res. Technol. 44 (2009) 985, DOI: 10.1002/crat.200900047

[8] V. Ramesh, K. Rajarajan, Crystal growth and characterization of a novel inorganic-organic hybrid NLO crystal: (NH4)[Cd(NCS)3]·C12H24O6, Appl. Phys. B, 113 (2013) 99, DOI: 10.1007/s00340-013-5444-z

[9] A.N. Chekhlov, Bis[(18-crown-6)potassium] tetrakis(isothiocyanato)zinc(II): synthesis and crystal structure, Russian J. of Inorg. Chem. 53 (2008) 780, doi:10.1134/S0036023608050185

[10] X.Q. Wang, D. Xu, M.K. Lu, D.R. Yuan, S.X .Xu, Mater Res Bull 36(2001), 879.

[11] H. Zhang, X. Wang,H. Zhu,W. Xiau, B.K. Tes, Inorg.Chem. 38 (1999) 886.

Cite the paper

K. Showrilu, V. Naga Lakshmi, K. Rajarajan, (2017). Synthesis, Growth and Characterization Aspects of Non-linear Organometallic Single Crystals of BCTZ. Mechanics, Materials Science & Engineering, Vol 9. Doi 10.2412/mmse.82.69.288