

International Journal of Scientific Research and Reviews

Enhanced Thermal, Dielectric and Nonlinear Optical Studies on Rhodamine B Doped BTCC Crystals for Nonlinear Optical Applications

M.Kalaiselvan¹, B.Latha², C.Tamilmalar³ and P.Kumaresan^{3*}

^{1,2,3,4} P.G & Research Department of Physics, Thiru.A.Govindasamy Government Arts College, Tindivanam - 604 307, Tamil Nadu, India.

² Department of Physics, Rajalakshmi Engineering College, Thandlum, Chennai, Tamil Nadu, India. Email : logeshkumaresan@yahoo.com

ABSTRACT

Pure and Bis Thiourea Cadmium Chloride (BTCC) crystals were grown by the slow cooling method and their lattice vibration and thermal properties were studied. Growth of pure and Rodamine B doped BTCC crystals and their characterization have been investigated. In view of finding good quality BTCC crystal, in the present investigation, an attempt has been made to grow an optical quality doped BTCC by low temperature solutions growth technique. The optical, mechanical and non-linear optical properties of the dye doped crystals were analyzed with the characterization studies such as powder XRD, FT-IR, UV-Visible, thermal, hardness, and dielectric and SHG measurements.

KEY WORDS: BTCC crystal, FT-IR studies, Dielectric Studies, Hardness Studies and SHG measurements

***Corresponding author:**

P. Kumaresan

P.G & Research Department of Physics,
Thiru. A. Govindasamy Government Arts College,

Tindivanam - 604 307, Tamil Nadu, India

1. INTRODUCTION

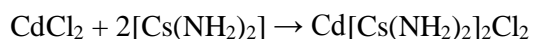
Non-linear optics playing a vital role in the emerging photo electronic technologies. New non-linear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical data storage^{1,2,3,4,5}. The search for new and efficient NLO materials has resulted in the development of a new class of materials called semi-organics. These materials have the potential for combining the high optical nonlinearity and chemical flexibility of organic materials with the thermal stability and mechanical robustness of inorganic NLO materials⁶.

Single crystals of pure and Rhodamine B doped Bis thiourea cadmium chloride (BTCC) are used extensively and have vast demand in the electronic industry as polarization filter, electronic light shutter, electronic modulator, optical voltmeter and as elements of electro-optic and electro-acoustic devices⁷. The origin of nonlinearity in NLO materials arises due to the presence of delocalized π -electrons system. Donor and acceptor groups connection are responsible for enhancing their asymmetric polarizability⁸.

2. EXPERIMENTAL PROCEDURE

2.1. Crystal growth

Slow evaporation technique was employed for the growth of BTCC crystals. BTCC salt was synthesized by dissolving AR grade thiourea and cadmium chloride in the molar ratio 2:1 in deionized water. The required amount of cadmium chloride and thiourea was estimated according to the following reaction:



The solution was heated and left for slow evaporation until the solvent completely dried and white crystalline salt was obtained. The salt was subjected to repeated recrystallization process. A solution of BTCC was continuously stirred using a magnetic stirrer of room temperature. The prepared solution was filtered and kept undisturbed in a constant temperature bath maintained at a temperature of 40°C. When evaporation taken place slowly, supersaturation is activated. As a result, crystals with dimensions 6.5 × 3.5 × 2.5 mm³ were harvested in a period of 18 days. BTCC crystals were grown from aqueous solution by slow evaporation method. The solubility of dyes doped BTCC in water was measured. It was found to be 15.5 g/100 ml at 38°C for Rhodamine B doped BTCC. The amount of BTCC salt to be dissolved was determined from its solubility curve at an average temperature of 38°C. The solution was stirred long enough to ensure complete dissolution of the solute, and filtered. Subsequently the solution was cooled at a rate of 0.1°C/day. The seed crystals

were prepared at low temperature by spontaneous nucleation (Figure 1). The seed crystals with perfect shape and free from macro defects were used for growth experiments. Seed crystals of pure BTCC and Rhodamine B doped BTCC were grown using constant temperature bath controlled with an accuracy of $\pm 0.01^\circ\text{C}$. A supersaturated solution of Rhodamine B doped BTCC was prepared in distilled, deionized water. Seed crystals were introduced into the solution using thin nylon thread at the appropriate super-saturation condition. Experiments were allowed to run for considerably longer duration of the time (18 days) would grow large crystals.

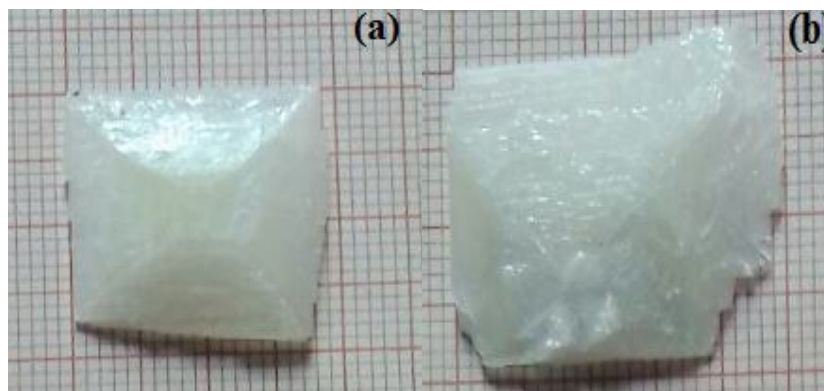


Figure 1. Photographs of (a) Pure and (b) Rhodamine B doped BTCC crystal

3. CHARACTERIZATION STUDIES

3.1. Powder X-ray diffraction analysis

Powder XRD studies were carried out for the grown crystals using a Rich Seifert X-ray diffractometer with CuK_α ($\lambda = 1.5405 \text{ \AA}$) radiation. Powder X-ray diffraction spectra of the grown crystals from pure and doped BTCC are shown in Figure 2. Powder XRD spectra for the pure and doped BTCC revealed that the structures of the doped crystals were slightly defected compared to the pure BTCC crystal. The (h; k; l) planes satisfy the general reflection conditions of space group were observed from the structure determination of the crystal. This may be attributed to strain on the crystal lattice by the absorption / substitution of dye. It is observed that the reflection lines of the dye doped crystal correlate well with those observed in the individual parent compound with a slight shift in the Bragg angle⁹.

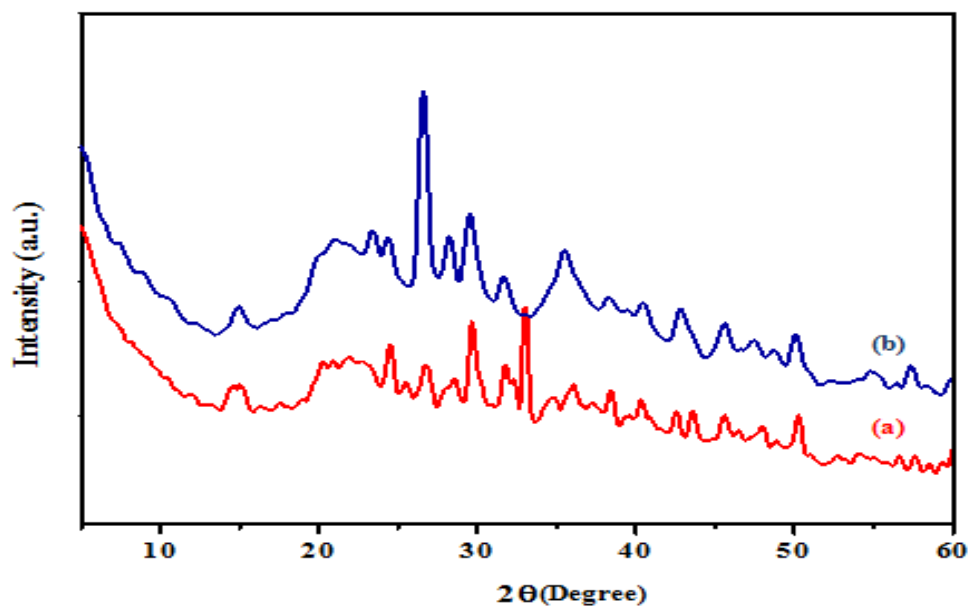


Figure 2. XRD Spectra of (a) pure BTCC crystal, (b) Rhodamine B doped BTCC crystal

This sample was scanned for 2θ values from 10° to 80° . The Lattice parameters were calculated by Least Square fit method and compared with reported studies. The crystal is in orthorhombic system with Pna21 space group. Powder X ray diffraction analysis confirmed crystalline nature of the grown crystal. The lattice parameters are $a = 5.121\text{\AA}$, $b = 7.532\text{\AA}$, $c = 15.389\text{\AA}$

3.2. UV-Visible studies

The UV-Visible transmission spectra were taken at room temperature using Varian Cary 2300 Spectrometer (UV-VIS-NIR), and they were recorded in the range 200-1200 nm for 1 mm thick C-cut plates of pure and Rhodamine B doped BTCC as shown in Figure 3. All the crystals irrespective of the dopant were transparent in the entire visible region. The UV-Visible spectrum of Rhodamine B doped BTCC crystal absorption (λ_{max}) spectrum was appeared at maximum wavelength of 785 cm^{-1} . Therefore, it reveals that the UV absorption was shifted to Red region, after incorporation of Rhodamine B dye.

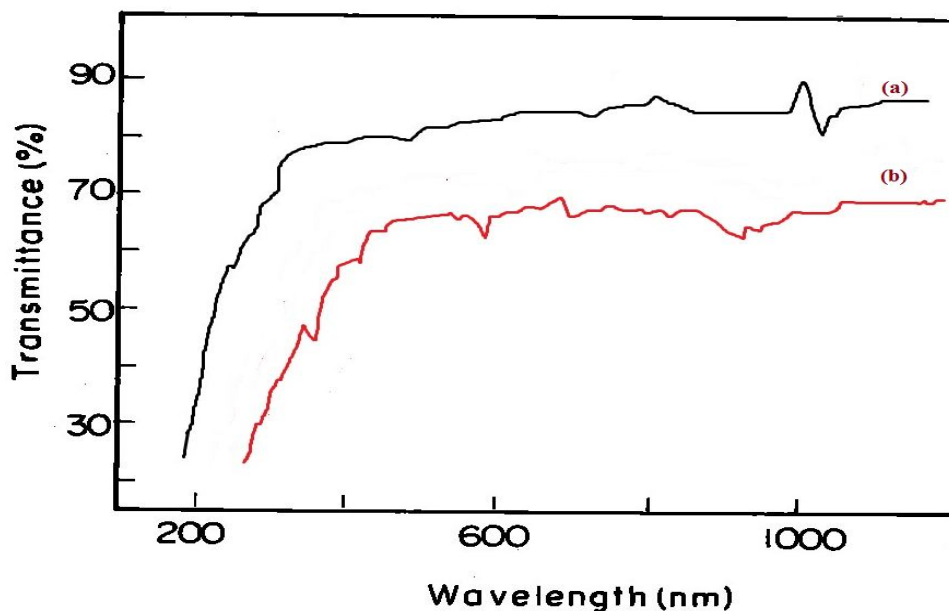


Figure 3. UV-Visible spectra of (a) Pure and (b) Rhodamine B doped BTCC crystal

The pure BTCC crystal has about 75 % of transmission. The dye doped BTCC crystal is invariably has higher transmission percentage compared to pure BTCC crystal. From the UV-Visible spectrum, the transmission percentage decreases due to addition of dopant with BTCC crystal, which would enhances the optical property of BTCC crystal.

3.3. FT-IR studies

The FT-IR spectra of pure and dyes doped BTCC crystals were analyzed using Bruker IFS 66V model spectrophotometer with 1064 nm output of a cw diode pumped in Nd:YAG laser as a source of excitation in the region $1000 - 4000 \text{ cm}^{-1}$ operating at 200 mW powers at the samples with a spectral resolution of 2 cm^{-1} . The observed FT-IR spectra of pure and doped BTCC are shown in Figure 4. In doped BTCC spectra, broad peak around 3650 cm^{-1} was due to free -OH stretching vibration^{10,11,12,13}. It reveals that at least one of the -OH group of BTCC was remain unaltered after doped with BTCC. Nitrogen containing thiocarbonyl group of glycine and that the C=S vibration was not located in the spectra¹⁴. FT-IR Due to the greater mass of sulphur in BTCC the C=S stretching vibration was expected to occur at 1024 cm^{-1} , it was considerably lower frequency than the usual C=O stretching vibration at 1710 cm^{-1} because of the C=S group is less polar than the C=O group and has a considerably weaker bond. The strong vibrational coupling studies of BTCC crystal were carried out in wave number range from 4000 to 450 cm^{-1} .

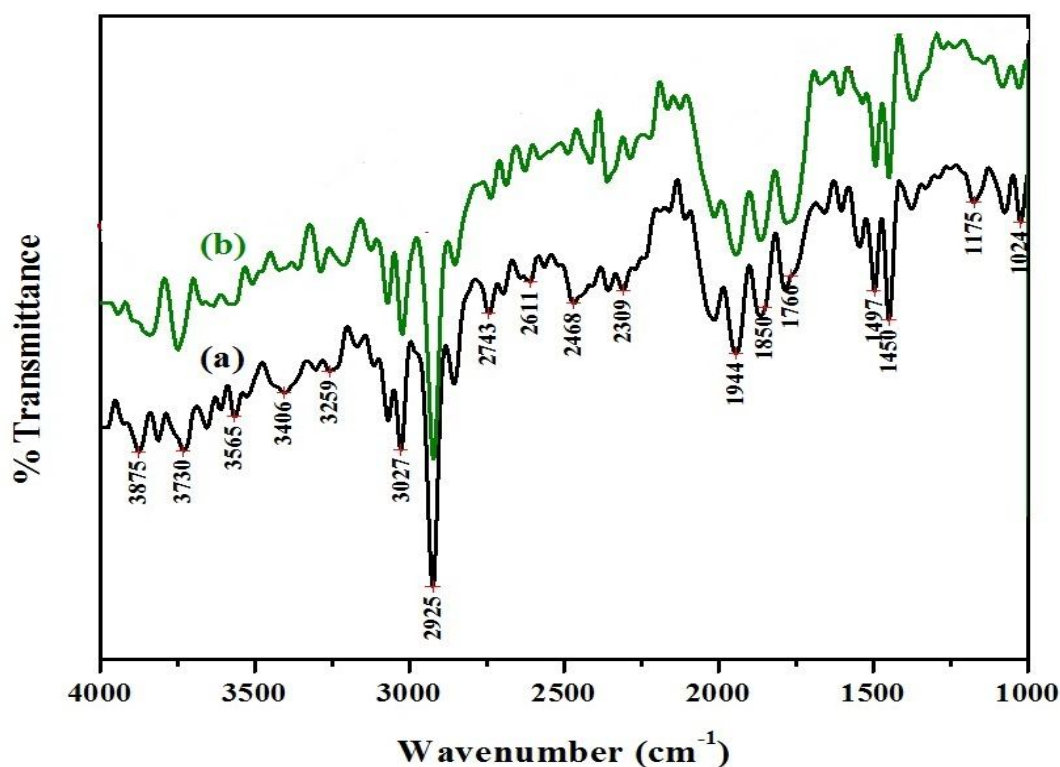


Figure 4. FT-IR spectra of (a) Pure and (b) Rhodamine B doped BTCC crystal

FT-IR spectra of Rhodamine B crystal is shown in Figure 4. The O-H asymmetric stretching produces the characteristic peak at 3027 cm^{-1} . Presence of band in the region $2925\text{--}3875\text{ cm}^{-1}$ is the characteristic region for the identification of C–H stretching vibrations. The comparison of FT-IR studies on pure and Rhodamine B doped BTCC crystals were tabulated in Table 1.

Table 1. FT-IR assignments of Pure and Rhodamine B doped BTCC crystals

Calculated frequency (cm^{-1})	Pure BTCC	Rhodamine B doped BTCC	Assignments
3875	3600(w)	3650(w)	Free O-H stretching
3565	-	3250(vw)	N-H asymmetric stretching
3100	3100(br)	-	Intramolecular H-bonded O-H stretching
2925	-	2900(br)	N-H symmetric stretching in NH_2 group
2611	2650(br)	-	O = P – OH asymmetric stretching of KDP
2250	2390(w)	2250(br)	P-O-H asymmetric stretching
1850	1650(br)	1650(vs)	O = P – OH symmetric stretching of KDP
1350	1300(sh)	1450(vs)	P=O symmetric stretching (aliphatic)
1150	1100(sh)	1170(vs)	P-O-H symmetric stretching
1024	985(s)	-	O = P – OH bending

3.4. Microhardness studies

The important mechanical properties were measured by the commonly used Micro hardness test for BTCC crystals. It can be suitably to measure the plastic properties and strength of a

material. Microhardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. The well-polished BTCC and doped BTCC crystals were placed on the platform of the Vickers micro hardness tester and the loads of different magnitudes were applied over a tester at some fixed time interval¹⁵. The indentation time was fixed as 8 sec for all the loaded crystals. The microhardness value was calculated using the relation $H_v = 1.8544 \times P/d^2$ kg/mm², where P is the applied load in kg and d is the diagonal length of the indentation impression in mm. Dye doping improves the mechanical strength of BTCC. Microhardness values of doped BTCC were tabulated in Table 2.

Table 2. Microhardness of Rhodamine B doped BTCC crystals

S.No	Crystal	Microhardness (kg/mm ²)
1.	BTCC	116.15
2.	Rhodamine B doped BTCC	173.56

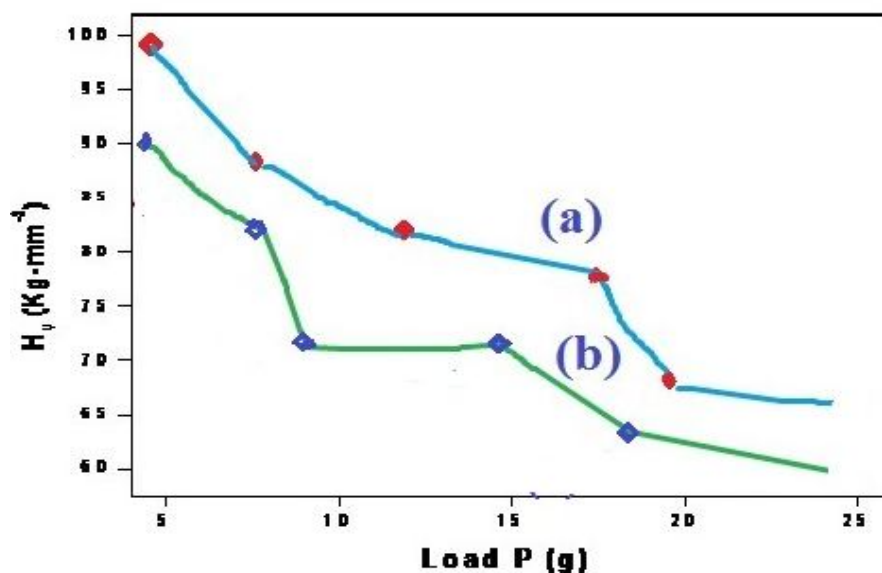


Figure 5. Microhardness studies of (a) Rhodamine B doped BTCC and (b) Pure BTCC crystals

Microhardness test is important to determine the mechanical strength of the materials and the resistance to local deformation. Mechanical properties such as elastic constant and yield strength can be determined from the hardness index (Figure 5). The hardness values are depends upon the quality of crystal polishing and for robustness of the device made out of the grown crystals.

Indentations were made with a Vickers’s hardness tester. The diagonals of the impressions were measured using a Leitz matallux II microscope with a calibrated ocular at magnification of x

500. The measurements were made at room temperature and the indentation time was kept at 8 seconds. The maximum indenter load applied was 50 g. Indentation with loads above 50 g led to micro cracks at the corners of the impressions made on the crystals^{16,17,18}.

The hardness of the crystals was calculated using the relation

$$H_v = 1.8544 \times P/d^2 \text{ kg/mm}^2$$

Where H_v is the Vickers hardness number, P is the indentation load in kg and d is the diagonal length of the impression in mm. The microhardness value was taken as the average of the several impressions made. The reproducibility of the microhardness values are $\pm 0.5\%$. Microhardness values of pure and dyes doped BTCC are measured and it was found that the dyes doped BTCC were higher hardness values than other crystals^{19,20,21}.

3.5. Thermal studies

The decomposition, phase transition, melting point and weight loss of the grown crystals were determined by means of thermo gravimetric analysis (TGA) by using TAQ-500 analyzer. The weight loss and thermal stability were determined at a heating rate of 25°C/min for temperature range 50 to 900°C in nitrogen inert atmosphere. The thermograms are shown in Figure 6. The TGA curve shows the first endothermic peak at 217.11°C and second peak at 276.14°C for Rhodamine B doped BTCC crystal. This decomposition lead to a weight loss of about 28.90% which may be due to the liberation of volatile substances like sulphur oxide²². In the case of pure BTCC crystal the endothermic peaks are at 218.24°C and 259.54°C with a weight loss of about 29.58%. There is no decomposition and phase transition up to the temperature 218.24°C in pure and 217.11°C in doped BTCC crystal. This ensures that the thermal stability of Rhodamine B doped BTCC crystal is higher than pure BTCC crystal. In both the grown crystals there is no weight loss up to 100°C, indicating absence of water in the molecular structure of the grown crystals. This temperature range of the grown crystals ensures the possibility of the crystals for NLO applications²³.

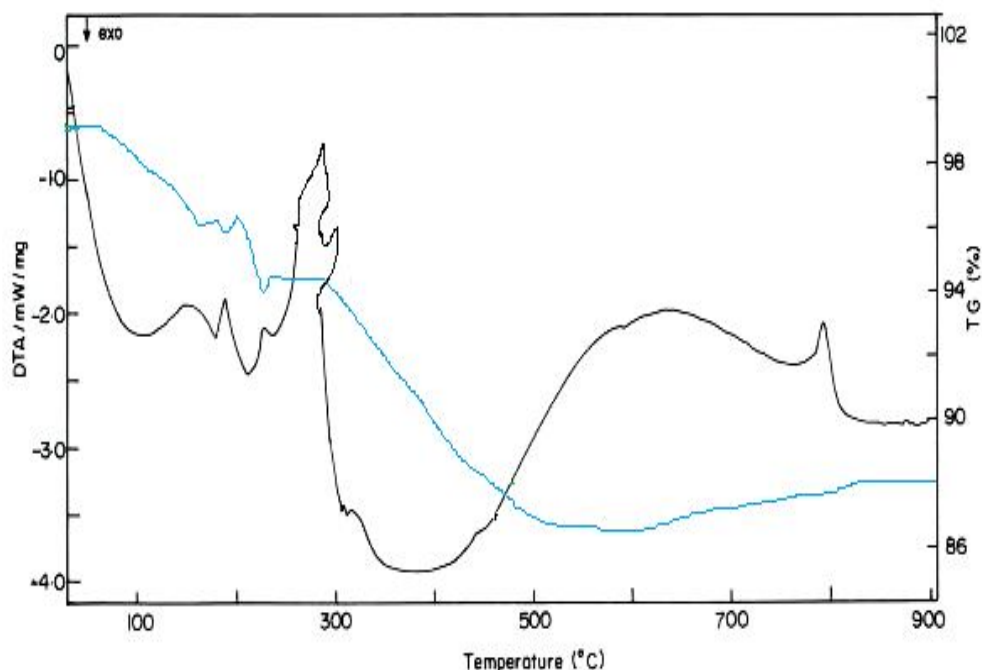


Figure 6. TGA-DTA curves of Rhodamine B doped BTCC crystal

The DTA curve implies that the material undergoes an irreversible endothermic transition at 200°C where the melting begins²⁴. This peak was endothermic peak, represents the temperature at which the melting terminates which corresponds to its melting point at 211°C. Ideally, the melting point of the trace corresponds to a vertical line. The sharpness of the endothermic peak shows good degree of crystallinity of the grown ingot. The exothermic peak at 292°C indicates a phase change from liquid to vapour state as evident from the loss of weight of about 85% in TG curve^{25,26,27}.

3.6. Dielectric studies

The dielectric study was carried out using Digital Lcrz Meter, TH2816A in the range of frequencies between 50 Hz-200 KHz. Good quality crystals were selected and polished by soft polishing pad with fine grade alumina powder. The face of single crystal was cut in to rectangular shape and well polished, so that it behaves as a parallel plate capacitor. Silver paste was used for making the electrode plates on these surfaces of the crystal. The samples were dried after electrode preparation to remove moisture. The dielectric constant ϵ_r was calculated using the relation²⁸.

$$\epsilon_r = Cd/\epsilon_0A$$

Where 'C' is the capacitance 'd' is the thickness of the crystal, ' ϵ_0 ' is the permittivity of free space and 'A' is the area of the crystal sample.

The capacitance of the crystal was measured to find out the relative dielectric constant. The sample was placed inside the dielectric cell. Figure 7 shows the dependence of dielectric constant

and dielectric loss on frequency. The large value of dielectric constant at low frequency is due to the presence of space charge polarization. The low value of dielectric loss reveals that the crystal has slightly defects. It was observed that the capacitance decreases with increase in frequency and this is due to charge redistribution^{29,30,31}.

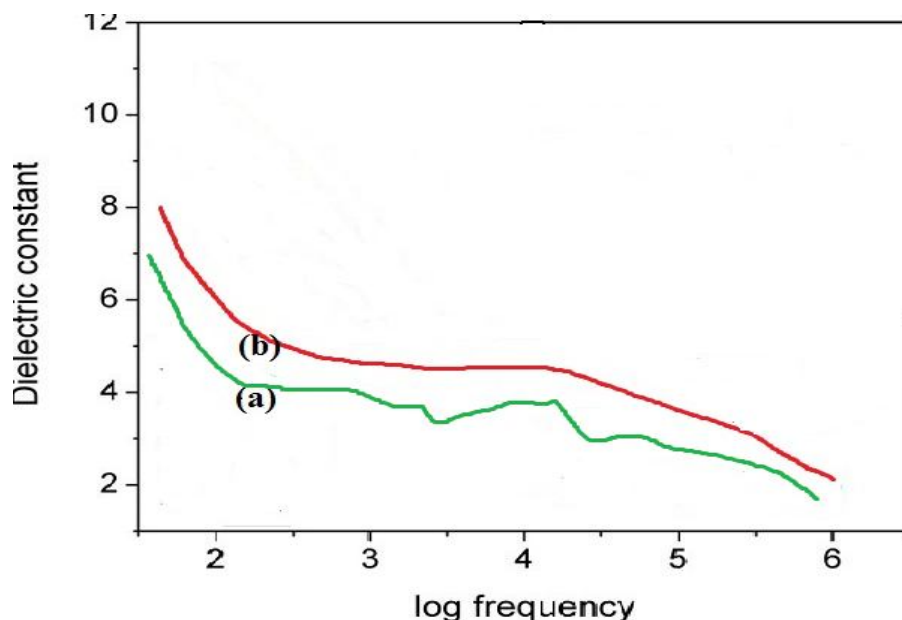


Figure 7. Dielectric studies of (a) Pure and (b) Rhodamine B doped BTCC crystal

The residuals present in the title compound act as mesoscopic capacitors that can acquire multiple charges of either sign³². At low frequency the residual charges more readily redistribute to the positive side of the applied field and become negatively charged, while the residues close to the negative side of the applied field become positively charged since the capacitance of the parallel plate capacitor is inversely proportional to the applied electric field. As the frequency increases the capacitance decreases and the charges no longer have time to rearrange in response to the applied voltage³³.

3.7. NLO studies

The Rhodamine B doped BTCC crystals are used for the generation of second harmonics by Nd-based near-infrared solid-state lasers. The fundamental of an Nd:YAG laser (1064 nm) can be converted to 532 nm of second harmonic or its 355 nm of third harmonic or its 266 nm of fourth harmonic by using Rhodamine B crystals^{34,35}. The performance of these frequency conversion devices can be seriously degraded, if there are any defect-associated, the absorption bands in the crystal which overlap the fundamental pump wavelength or one of the output wave lengths. Thus, it

is important to identify and characterize all potentially harmful absorption bands in non-linear optical crystals.

The dye doped BTCC crystals are used for the generation of second harmonics of Nd-based near-infrared solid-state lasers. Measurements were made using the Kurtz and Perry powder method. Schematic representation of the SHG setup is shown in Figure 8. The fundamental of an Nd : YAG laser (1064 nm) can be converted to 532 nm of second harmonic or its 355 nm of third harmonic or its 266 nm of fourth harmonic by using BTCC crystals. The performance of these frequency conversion devices can be seriously degraded if there are defect-associated absorption bands in the crystal which overlap the fundamental pump wavelength or one of the output wavelengths. Thus, it is important to identify and characterize all potentially harmful absorption bands in non-linear optical crystals. In order to confirm the suitability of the doped BTCC crystal, the non-linear applications, harmonic generation was tested using the Nd-YAG laser.

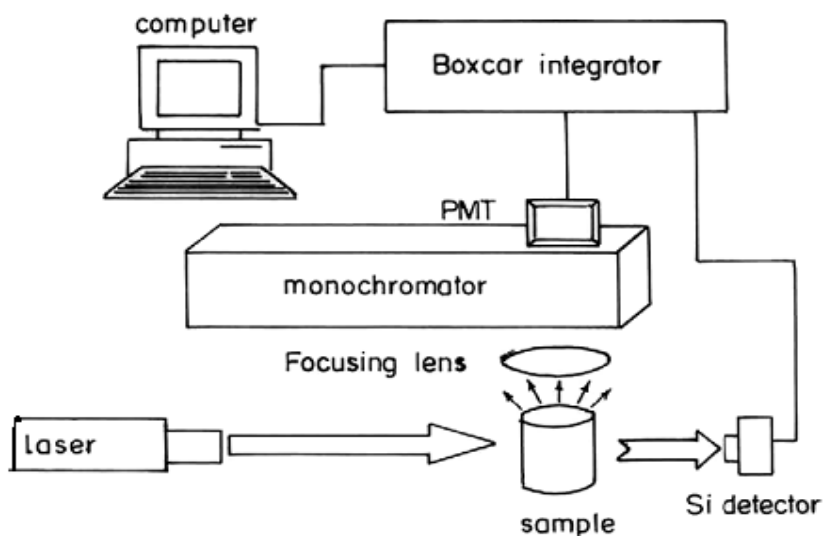


Figure 8. SHG Setup

Any second-harmonic produced was passed through a series of neutral density filters (Wratten, 1.0 + 0.7), then focused into a monochromator (Beckman DU spectrophotometer, model 2400) in order to discriminate between SHG light and stray visible light and IR light. Monochromatic 532 nm light was then directed on to a second photomultiplier (RCA IP28) for measurement.

The efficiency of doped BTCC crystals were compared with pure BTCC and also show that dye doped BTCC crystal has higher efficiency. A sample of BTCC, also powdered was used for the same experiment as a reference material in the SHG measurement. It was found that the

frequency doubling efficiency of the doped BTCC is better than KDP. A comparison of SHG property of BTCC crystal with dye doped BTCC crystal is presented in Table 3.

Table 3. Comparison of SHG of pure and Rhodamine B doped BTCC crystal

S.No.	Compound	SHG efficiency relative with KDP
1.	Pure BTCC crystal	1.68
2.	Rhodamine B doped BTCC crystal	1.97

The nonlinear property of the grown BTCC crystal was tested by passing the output of Nd:YAG Quanta ray laser emitting 1064 nm, generating about 6 mJ per pulse. The details of the experimental set-up are already discussed in previous Chapters. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.155 mm. The light emitted by the sample was detected by photodiode detector and oscilloscope assembly. The SHG efficiency of BTCC was determined by Kurtz and Perry powder technique. Microcrystalline materials of KDP were used for comparison with BTCC for Second Harmonic Generation experiments. For a laser input of 6.2 mJ, the second harmonic signal (532 nm) of 91.66 mW, 272.12mW and 438.39 mW were obtained for KDP, pure BTCC and dye doped BTCC respectively. The SHG efficiencies of pure and doped crystals are higher than that of KDP. Thus, the dye has increased the efficiency of pure BTCC.

4. CONCLUSION

Pure and Rhodamine B doped BTCC single crystals have been grown with reasonable growth rate along three crystallographic directions by solution growth method at room temperature. The lattice parameters have been found by single crystal X-ray diffraction technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The crystals are transparent in the visible and near infrared spectral regions. Optical transmittance of the crystals is 85%. Thermo gravimetric analysis shows that the grown crystals are thermodynamically stable upto 216°C. The Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. The SHG output voltage measured for pure and Rhodamine B doped BTCC crystals are higher than KDP. Thus the grown crystals are best suitable for NLO applications.

REFERENCES

1. P. M. Ushasree, R. Muralidharan, R. Jayavel, P. Ramasamy, *J. Cryst. Growth*, 2000; 218 :365-371.
2. J. Nyvlt, R. Rychly, J. Gottfried and V. Wurzelova, *J. Cryst. Growth*, 1970 ;6: 151-155.
3. D. Balasubramanian, R. Sankar, V. Siva Sankar, P. Murugakoolthan, P. Arulmozhichelvan, R. Jayavel, *Mater. Chem. Phys.* 2007;10:1016-1018.
4. K. Sangwal, *Pro. Crystal Growth. Cha.-19* ,1989,189.
5. B. Latha , P. Kumaresan, S. Nithiyantham , K. Sambath kumar, *Journal of Molecular Structure*, 2017; 1142: 255-257.
6. K. Srinivasan, S. Anbukumar and P. Ramasamy, *J. Cryst. Growth*, 1995 ;151: 226-229.
7. B. W. Mott, *Micro-Indentation Hardness Testing*, Bulterworths, London, 1956: 206-209.
8. P.A. Angeli Mary, S. Dhanuskodi, *Cryst. Res. Technol.* 2001; 13(36): 1231-1235.
9. R. Rajesekaran, P.M. Ushasree, R. Jayavel, P. Ramasamy, *J. Cryst. Growth*, 2001; 229: 563-567.
10. M. Oussaid, P. Becker, C.C. Nedelec, *Phys. Stat. Sol. (b)*1998; 207 : 499-502..
11. S.B. Monaco, L.E. Davis, S.P. Velsko, F.T. Wang, D. Eimerl, A. Zalkin, *J. Cryst. Growth*, 1987; 85: 252-255.
12. M. Lawrence, Thomas Joseph Prakash, *J. Spectrochimica Acta Part A* 2012 ;91: 30-34.
13. K. Sambathkumar, *Elixir Vib. Spec.* 2016; 913:8381-8385.
14. J.J. Jang, S.J. Luo, L. Yi and A. Laref, *Physica B. Condensed Matter.*, 2013;408: 175-176.
15. R. T. Bailey, F. R. Cruickshank, P. Kerkoc, S. Lochran, D. Pugh, J. N. Sherwood, A. J. Blake, and S. Parsons, *J. Appl. Phys.* 1995;78:3102-3106.
16. Kuppusamy Sambathkumar, *Spectrochim. Acta A* , 2015;147:51-66.
17. K. Sambathkumar, S. Nithiyantham, *J Mater Sci: Mater Electron*,2017; 28:6529-6543.
18. T. Wojtatowicz and K. Rozniakowski, in *Thermal Conductivity 20*, edited by D. P. H. Hasselman and J. R. Thomas, Jr. Plenum, New York, 1989; 367–375.
19. G. Xing, M. Jiang, Z. Sao, D. Xu, *Chin. J. Lasers*, 1987; 14:302-308.
20. P. Kerkoc, V. Venkataraman, S. Lochran, R.T. Bailey, F.R. Cruickshank, D. Pugh, J.N. Sherwood, *J. Appl. Phys.* 1996; 80: 6666-6669.
21. P.M. Ushashree, R. Jayavel, C. Subramanian, P. Ramasamy, *Bull. Electrochem.* 1998 ;14: 407-410.
22. P.M. Ushashree, R. Jayavel, *Optical Materials*, 2003; 21(1):599-604.
23. S.K. Kurtz, T.T. Perry, *J. Appl. Phys.* 1968; 39 :3798-3813.

24. 24. S. Selvakumar, J. Packiam Julius, S.A. Rajasekar, A. Ramanand, P. Sagayaraj, Mater. Chem. Phys. 2005 ;(89):244-248.
25. 25. V. Venkataramanan, C.K. Subramanian, H.L. Bhat, J. Appl. Phys. 1995 ;(77): 6049-6052.
26. 26. Pricilla Jeyakumari, J. Ramajothi, S. Dhanuskodi, J. Cryst. Growth, 2004 ;(269):558-564.
27. 27. N.R. Dhumane, S.S. Hussaini, Kunal Datta, Prasanta Ghosh and Mahendra D. Shirsat, J. Pure Appl. & Ind. Phys., 2010;(1):45-52.
28. 28. Angeli Mary PA, Dhanuskodi S, Cryst. Res.Techol., 2001; (36) : 1231-1237.
29. 29. Arriponnammal S, SelvaVennila R, Radhika S, Arumugam S, Cryst. Res. Techol., 2005; 40(9):896-897.
30. 30. Dhunane NR, Hussaini SS, Dongre VG, Karmuse PP, Shirsat MD Cryst. Res. Techol., 2009, 44(3):269-274.
31. 31. Kushwaha SK, Vijayan N, Bhagavanna G Materials Letters, 2008; 62(24): 3931-3933.
32. 32. Lydia CM, Vasudevan S Mater.Chem. Phys., 2009; 113:670-674.
33. 33. Moritra S, Kar T, Opt. Mater., 2008 ;(30)1621-1624.
34. 34. Pricilla JA, Ramajothy J, Dhanuskodi S J. Cryst. Growth, 2004; (269):558-564.
35. 35. P. Sivakala, N. Joseph John and S. Perumal , Int. Journal of Engineering Research and Applications, 2014;4(7):145-151.