IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 2, Issue 1, December 2022
Impact Factor: 6.252

Development of Functional Single Crystals for Laser Communication and Integrated Optics

Dr. Vipin Kumar
Department of Chemistry
H.N.B. Government Post Graduate College, Naini, Prayagraj, Uttar Pradesh, India
vipinktiwari2010@gmail.com

Abstract: *Within the past hundred years, the optical crystal area has passed through a rapid evolution- from the discovery of naturally occurring crystals to the creation of sophisticated synthetic materials specifically designed to meet the demands imposed by modern technology. Non- linear optical crystals have a great impact on information technology and industrial applications. The dielectric analysis is an important characteristic that can be used to fetch knowledge on the electrical and ionic properties of a material medium as a function of temperature and frequency. The second harmonic generation values of the single crystals are useful in optical communication and signal processing in integrated optics. The present paper deals with the growth and characterization of Thiourea based crystals namely Thiourea Cadmium Chloride (TCC), Thiourea Cadmium Bromide (TCB), and Thiourea Zinc Sulphate (TZS). The single crystals were grown by slow evaporation technique at room temperature. Powder XRD pattern reveals the single crystalline nature of the crystals. FTIR studies confirm the functional groups in the crystals. The optical transparency of the crystals was determined by UV- Visible studies. The grown single crystals were also subjected to dielectric and Non linear optical (NLO) Second harmonic generation (SHG) measurements. The dielectric and optical studies carried out reveal that the TCC, TCB, TZS crystals exhibit good optical quality and possible NLO applications.*

Keywords: NLO, XRD, SHG, dielectric studies

I. INTRODUCTION

Crystal growth plays an important role in modern technology. Crystals are the solids in which the elementary building blocks, the atoms are arranged regularly in a space lattice with specific geometrical symmetry. Single crystals find a wide range of applications in laser technology, optoelectronics, light emitting diodes, thermography etc, therefore growth of single crystals is of at most importance for further development in materials research. Non linear optical crystals are widely used in modern optical science and technology for frequency conversion of laser light, i.e., to generate laser radiation at any specific wavelength in visible, Ultraviolet or infrared spectral regions.

In the present work Thiourea cadmium chloride (TCC), Thiourea cadmium bromide (TCB) and Thiourea zinc sulphate (TZS) single crystals were grown by slow evaporation method. The grown crystals were characterized by single and powder X- Ray diffraction studies (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Visible, Dielectric and Non linear optical (NLO) studies.

II. MATERIALS AND METHODS

The single crystals of TCC, TCB and TZS were grown by slow evaporation technique at room temperature. The ratio in which the constituent compounds were added in each case were 1:1 respectively. A saturated solution of the salts were prepared and filtered. The filtered solutions were transferred to Petri dishes which were closed with thick papers with fine pores in order to minimize the rate of evaporation. The solutions were allowed to evaporate completely and the single crystals of TCC, TCB and TZS were harvested.

IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 2, Issue 1, December 2022
Impact Factor: 6.252

The cell parameters and geometry of the grown single crystals of TCC, TCB and TZS were determined by Single XRD analysis using ENRAF NONIUS CAD4 diffractometer.

The grown single crystals of TCC, TCB and TZS were subjected to Powder XRD analysis using Rich Seifert X-ray diffractometer with Cu Kα ($\lambda = 1.5406$Å) radiation. The samples were scanned for 2θ values from 10˚ to 60˚ at a rate of 2˚ /min.

The FTIR analysis of the single crystals of TCC, TCB and TZS were carried out using a BRUKER IFS 66V model spectrophotometer by KBr pellet method in the wave-number range of 4000 to 450 cm-1.

UV- visible spectral study is a useful tool to determine the transparency which is an important requirement for a material to be optically active. The optical transmittance spectrum of the grown crystals of TCC, TCB and TZS of thickness 2 mm were recorded in the wavelength range 200- 800 nm using Cary 5E UV-Vis-NIR Spectrophotometer.

Dielectric measurements of grown single crystals of TCC, TCB and TZS were carried out using HIOKI 3532-50 LCR HITESTER in the frequency range 50 Hz to 5 MHz. A sample of crystal having silver coating on the opposite faces was placed between two copper electrodes to form a parallel plate capacitor and measurements were made. The dielectric constant and dielectric loss were measured and plotted for frequencies 50 Hz to 5 MHz at three different temperatures 313 K, 323 K, 333 K. The dielectric constant of the grown single crystals of TCC, TCB and TZS were calculated using the formula where, C is the Capacitance of the sample, d the Thickness, A is the Area of the sample and εo is the permittivity of free space.

Kurtz second harmonic generation (SHG) test was performed to find the NLO property of the TCC, TCB and TZS single crystals. The crystals were ground into powder and densely packed in between two glass slides. A Q-Switched Nd: YAG laser beam of pulse width 8 ns at a wavelength of 1064 nm and 10 Hz fundamental radiation was made to fall normally on the sample cell and measurements were carried out.

$$\varepsilon r = \frac{C \times d}{A \times \varepsilon 0}$$

II. RESULTS AND DISCUSSION

Good quality single crystals of TCC, TCB and TZS were harvested, the details of which are listed in Table 1.

Table 1: Growth details of TCC, TCB and TZS single crystals

S.No	Crystal	Constituent Compounds	Growth period	Crystal Size
1.	TCC	Thiourea and Cadmium chloride	8 days	0.4 cm X 0.6 cm
2.	TCB	Thiourea and Cadmium bromide	8 days	0.1 cm X 1 cm
3.	TZS	Thiourea and Zinc sulphate	8 days	0.5cm X 0.6cm

Figs 1, 2 and 3 represent the photographs of as grown crystals of TCC, TCB and TZS.

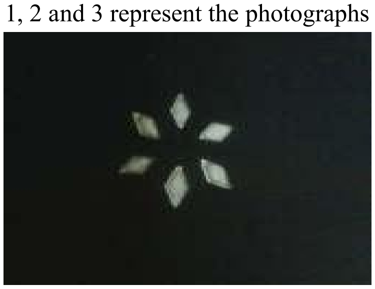

Figure 1: As grown crystals of TCC

Figure 2: As grown crystals of TCB

Figure 3: As grown crystal of TZS

Single XRD

Single crystal X-ray diffraction (XRD) is a non- destructive tool to analyze crystal structure of compounds, which can be grown as single crystal;

ISSN 2581-9429 IJARSCT

IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 2, Issue 1, December 2022
Impact Factor: 6.252

From the studies it was found that TCC, TCB and TZS single crystals belong to orthorhombic system. The lattice parameter values of the grown single crystals are listed in table 2.

Table 2: Lattice parameter values of TCC, TCB and TZS

Crystal	a (A0)	b (A0)	c (A0)	α= β= γ
TCC	5.80	6.74	13.05	900
TCB	5.97	12.97	13.45	900
TZS	7.78	11.158	15.497	900

Powder XRD

The prominent peaks obtained in the powder X- ray diffraction patterns (Figs 4, 5 and 6) of the grown crystals of TCC,TCB and TZS confirm the single crystalline nature of the grown crystals.

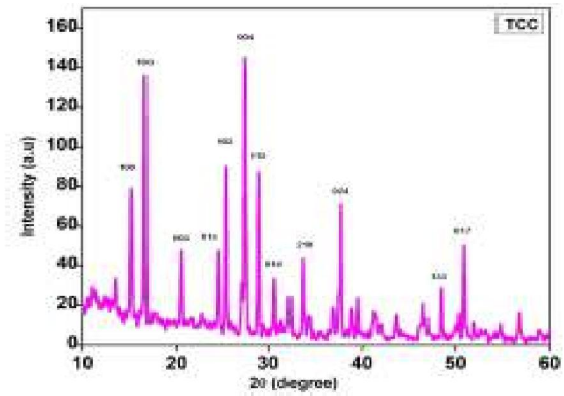

Figure 4: Powder XRD pattern TCC

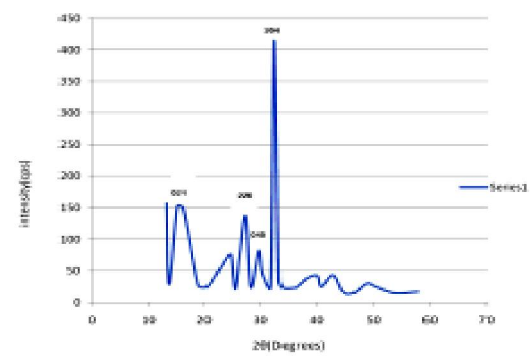

Figure 5: Powder XRD pattern TCB

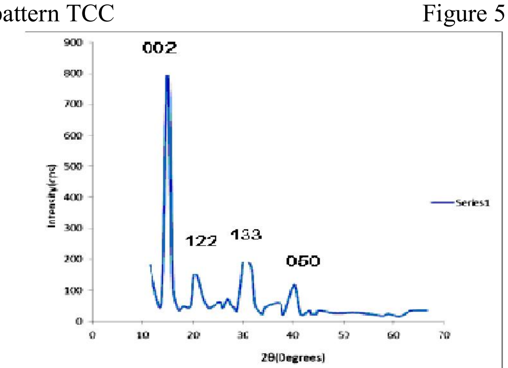

Figure 6: Powder XRD pattern TZS

FTIR Studies

The functional groups present in the single crystals of TCC, TCB and TZS were identified with the help of available data and presented in the table 3.

Table 3: Various functional groups of TCC, TCB and TZS

Crystal	Wavenumber (cm^{-1})	Band Assignment
	3390	N-H stretching
	3285	Asymmetric NH_2 stretching
	1614	C=S stretching
	1495	NH_2 bending

ISSN 2581-9429 IJARSCT

IJARSCT
ISSN: 2581-9429
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
Volume 2, Issue 1, December 2022
Impact Factor: 6.252

TCC	1434	NH_2 bending
	1395	NH_2 bending
	1100	C-N vibration
	715	C=S stretching
	480	N-C-N bending
TCB	3382	N-H stretching
	3280	NH_2 Asymmetric stretching
	3167	NH_2 symmetric stretching
	1382	C=S Asymmetric stretching
	1090	CN symmetric stretching
	474	NCN symmetric bending
TZS	3376	NH_2 stretching
	3198	NH_2 symmetric stretching
	1626	NH bending
	1503	N-C-N stretching
	1122	N-C-N stretching
	1031	C=S asymmetric stretching
	792,1400	C=S symmetric stretching
	618	S-O stretching
	474	S-C-N symmetric bending

UV- Visible Studies

The UV- Visible spectrum of the single crystals of TCC, TCB and TZS (Fig 7, 8 and 9) indicate Low absorption in the entire visible and near infrared region of the crystals. This is a desirable property for NLO applications since a wider optical transparency in these regions enhances the frequency conversion efficiency in the corresponding wavelengths.

The lower cut off wavelengths of TCC, TCB and TZS single crystals were found to be 258 nm, 254 nm and 260 nm respectively. The optical band gap of TCC, TCB and TZS single crystals were determined to be 4.81 eV,4.88 eV and 4.77 eV respectively.

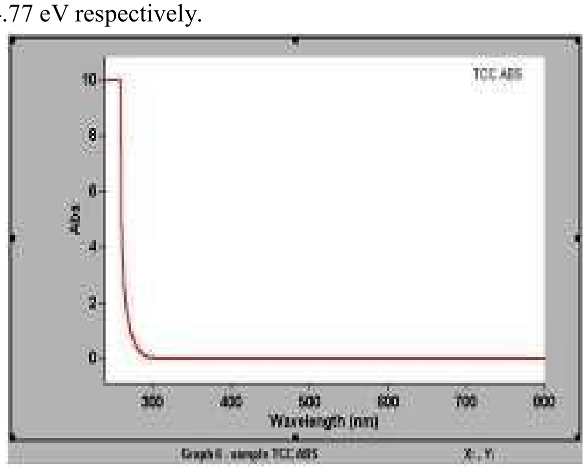

Figure 7: UV- Visible spectrum TCC

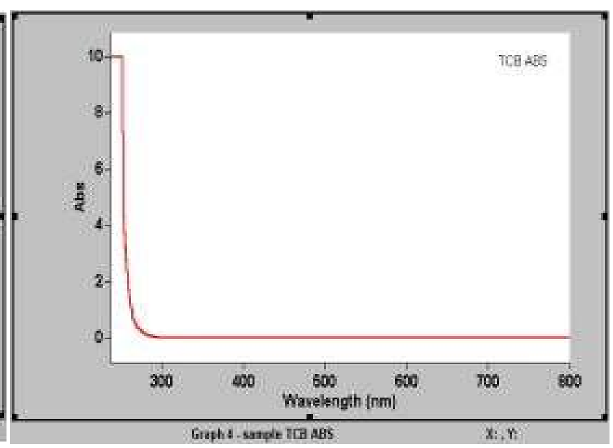

Figure 8: UV- Visible spectrum TCB

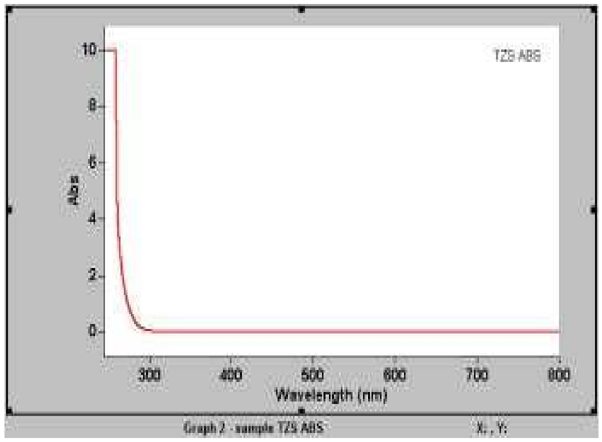

Figure 9: UV- Visible spectrum TZS

Dielectric Studies

TCC

The dielectric constant of TCC is high at lower frequencies and subsequently shows a sharp decrease, attaining almost a constant value in the high frequency region (Fig 10). The dielectric loss shows considerable fluctuations at high frequencies due to the variation of the relaxation times for different polarization processes. The peak values of dielectric constant and dielectric loss decrease with increasing temperature which may be attributed to the temperature variation of ionic polarizability.

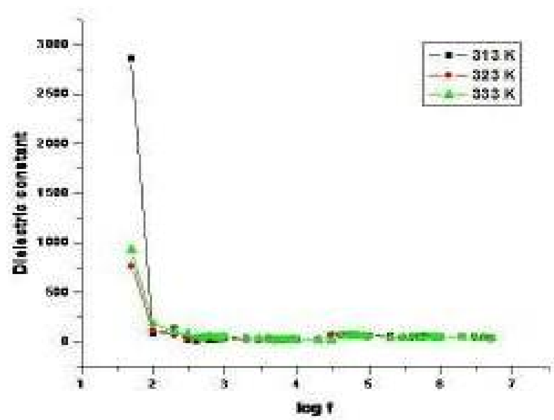

Figure 10: Dielectric constant Vs frequency (TCC)

TCB

The dielectric constant (Fig 11) and dielectric loss of TCB is high at lower frequencies and decreases sharply, attaining a constant value as the frequency is increased. The very high value of dielectric constant observed at low frequencies, is due to the presence of all the four polarizations namely; space charge, orientation, electronic and ionic and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. When the electric charge carriers cannot follow the alternation of the ac electric field applied beyond a certain critical frequency, the dielectric constant decreases with increasing frequency and remains constant

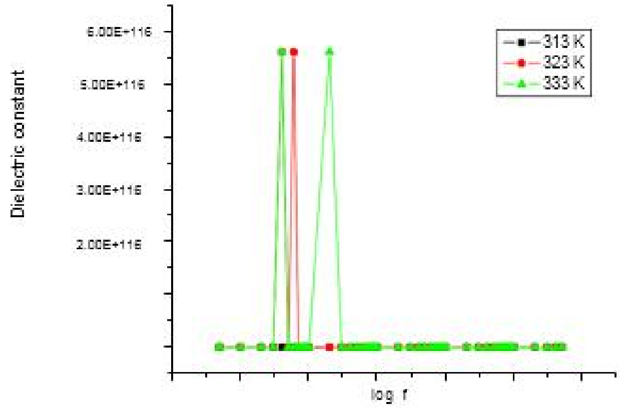

Figure 11: Dielectric constant Vs frequency (TCB)

TZS

The dielectric constant of TZS decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region (Fig 12). The dielectric loss is strongly dependent on the frequency of the applied field similar to that of dielectric constant.

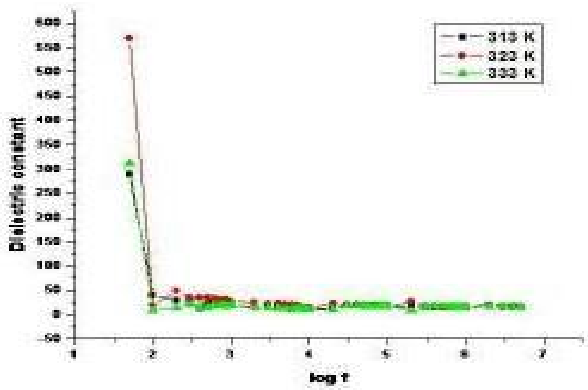

Figure 12: Dielectric constant Vs frequency (TZS)

The dielectric studies of TCC, TCB and TZS single crystals indicate low value of dielectric constant at higher frequency. This suggests that the samples possess enhanced optical quality with lesser defects and this parameter is of vital importance for various NLO applications.

NLO Studies

The second harmonic signal, generated in the crystals was confirmed from the emission of green radiation by the crystals. The NLO SHG values of the TCC,TCB and TZS single crystals were determined and compared to the reported SHG value of pure KDP (Table 4)

Table 4: NLO SHG data for TCC, TCB, TZS single crystals

S.No	Crystal	Second harmonic signal output (mJ)	SHG efficiency (compared to SHG efficiency of pure KDP)
1.	TCC	8.2	3
2.	TCB	1.8	0.64
3.	TZS	4.8	1.71

III. CONCLUSION

TCC, TCB and TZS single crystals have been grown by the slow evaporation solution growth technique. The single crystalline nature of the crystals is confirmed by powder X-ray diffraction. Single crystal X-ray diffraction studies reveal that TCC,TCB and TZS belong to the orthorhombic system . The UV-Vis absorption spectrum shows transmittance from the cut off wavelength 200 nm to 800 nm. The lower cut off for all the three samples were observed. The functional groups present in the samples were assigned by the FT-IR spectrum. The dielectric constant and dielectric loss studies of the single crystals of TCC, TCB and TZS establish their electrical behavior, good optical quality and their suitability for NLO applications. Kurtz-Perry powder SHG test was employed to determine the SHG efficiency of the samples and the values were compared to the reported SHG efficiency of pure KDP.

ACKNOWLEDGEMENT

The Author would like to thank IIT Delhi for their full fledged support in carrying out the characterization techniques.

REFERENCES

[1]. Balamurugaraj P., Suresh S. , Koteeswari P., Mani P.; 2013. Growth, Optical, Mechanical, Dielectric and Photoconductivity Properties of L-Proline Succinate NLO Single Crystal. JMPC, 1(1): 4- 8.

[2]. Balarew C, Duhlew R; 1984. Application of the hard and soft acids and bases concept to explain ligand coordination in double salt structures. J.Solid State Chem., 55(1): 1-6.

[3]. David Nikosgosyan N.; 2005. Non linear Optical Crystals: A Complete Survey . Springer publications: 10.

[4]. Delci Z., Shyamala D., Karuna S., Thayumanavan A.; 2012. Optical Characterization Studies on boron doped KDP crystals. Arch.Phy.Res., 3(5): 346-353.

[5]. John Coates; 2000. Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry. John Wiley and Sons Ltd, Chichester : 10815- 10837.

[6]. Kumararaman S., Cicili Ignatius I., Thaila T., Raja T., Selvaraju K.; 2012. Growth, spectroscopic, thermal and hardness studies of urea thiourea zinc iodide crystal as potential NLO material Arch.Appl.Sci.Res., 4(6): 2467-2473.

[7]. Palanisamy Saritha, Seshathri Bharathan, Ganesan Sivakumar; 2013. Growth and Analysis of Urea Thiourea Sodium Sulphate Crystal .IOSR-JAP, 4(4): 38-41.

[8]. Revathi V., Rajendran V.; 2012. Synthesis, Growth and characterization of semi-organic zinc (tris) thiourea chloride crystal .RRST, 4(2), 38- 41.

[9]. Sagadevan Suresh; 2012. Techniques and tools used for investigating the grown crystals: A review. Lat.Am.J.Phys.Educ., 6(4):547-558.

[10]. Silverstein R.M., Clayton Basseler G., Morrill T.C.;1998. Spectrometric Identification of Organic Compounds. V-Ed. John Wiley and Sons, Inc, New York: 45.Uma Maheswaria R., Joseph Arul Pragasama A.;2013. Growth and Electrical Properties of Thiourea Doped l-threonine NLO Single Crystal. PIJR, 2(11), 254-255.