Original Research Article

INVESTIGATIONS ON THE OPTICAL, THERMAL, ELECTRICAL AND PIEZOELECTRIC PROPERTIES OF BIS THIOUREA CADMIUM CHLORIDE (BTCC) CRYSTALS

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ABSTRACT: The single crystals of dimension 15 x 15x 8 mm^3 of Bisthiourea cadmium chloride (BTCC) are synthesized from aqueous solution using slow evaporation technique at ambient temperature. High resolution X-ray diffraction technique is employed to estimate the crystalline perfection of the grown single crystals. The grown crystals are confirmed by CHN analysis. The UV cut-off wavelength is found to be 320 nm and the optical band gap of BTCCC crystals is measured to be about 3.75eV. The thermal parameters at a modulation frequency 40Hz such as Thermal effusively (e), Thermal diffusivity (α), Thermal conductivity (k), Heat capacity (C$_p$) of the BTCC crystals are measured. The electrical properties such as dielectric constant, dielectric loss and ac conductivity of the BTCC crystals are carried out by Agillent E 4980 A LCR meter at different temperatures. The piezoelectric charge coefficient is found to be 8 pC/N. The P-E loop of the BTCC crystal was analyzed and the loop parameters were measured.

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1. INTRODUCTION

During the past few decades researchers working in the field of nonlinear optics developed new organometallic compounds having appreciable second harmonic properties, improved laser damaged threshold and excellent optical nonlinearity when compared to the organic counterpart [1]. In 1987 Chinese scientists investigated metal organic compounds for nonlinear optical applications, based on the Double-radical model [2-4]. The insights of this research laid the foundation for our research group to start the study of a primary aspect of the nonlinear optical properties of the organometallic crystals. While giving credits to the these materials of Chinese researches as well as research carried out by the Indians, this study concentrates on experiments providing more insights into the nonlinear optical properties of the materials and their qualities that can be easily and economically made use in our day to day life. The materials showing high quality optical bistability are found to be applicable in optoelectronics. Thiourea crystals exhibit large dipole moment and ability to form extensive network hydrogen bonds [5]. When the centrosymmetric thiourea is joined with metals, it will produce large hyperpolarizability which in turn results high nonlinear optical properties. Materials researchers are fascinated by this nonlinear optical property in thiourea complexes and many crystals based on the thiourea were investigated. Motivated by this consideration, a lot of thiourea complex crystals were explored.   Recently, M $[tu]_2$ X_2 type materials are interested by researchers where M=Cd, Co, Hg, Pb, Ti and Zn, tu is thiourea and X is a halogen [6], because they exhibit good nonlinear optical properties. Bisthiourea cadmium chloride (BTCC) [7], bisthiourea zinc chloride (BTZC) [8], bisthiourea cadmium acetate (BTCA) [9] Zinc tris (thiourea) sulphate (ZTS), Allylthiourea cadmium chloride (ATCC) [10], allylthiourea cadmium bromide (ATCB) are some of the crystals of the above said type [11]. BTCC is superior to other organometallic crystals for researchers because of their extended transparency down to UV, high optical nonlinearity and moderate mechanical property. BTCC is 110 times more nonlinear than quartz [12]. The laser damage threshold of BTCC crystals is 32 GW/cm^2 and 6 GW/cm^2 for single and multiple shots respectively. From the earlier reports BTCC belongs to orthorhombic crystal structure with the space group $P_{mn}2_1$ and its unit cell contains four molecules. They have the large laser induced damaged threshold compared to the other NLO crystals [13,14]. Bis(thiourea) cadmium chloride (BTCC) is a good candidate for engineering, a material with high nonlinearity out of an organic ligand by metal complexation [15]. Hence the present study deals with the synthesis, growth and physicochemical properties of the BTCC crystals.

2. MATERIALS AND METHODS

Single crystals of Bisthiourea cadmium chloride (BTCC) were grown by the solution growth techniques. Analytical reagent (AR) grade of the cadmium chloride and thiourea along with millipore water were used for the growth process. BTCC was synthesized from aqueous solutions of $CdCl_2$ and thiourea in the ratio 1:2 following the chemical reaction.

$$CdCl_2 + 2CS(NH_2)_2 \rightarrow Cd[CS(NH_2)_2]_2 Cl_2$$
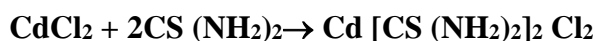
The pH value of the solution was adjusted to be 3 by adding hydrochloric acid with continuous stirring for few hours. The solution was heated and stirred well at room temperature to avoid the precipitation of multiple phases [16-18]. The purity of the synthesized salt was increased by successive re-crystallization process. Temperature as low as 50°C was maintained in order to avoid decomposition. The saturated solution was taken in a beaker covered it tightly and then it was allowed to evaporate at room temperature by making small holes on the top of the cover. Seed crystals of dimension 15 x 15 x 8 mm^3 were hatched out due to spontaneousnucleation, within a period of around one month. The photographs of as grown crystals were shown in Fig.1.
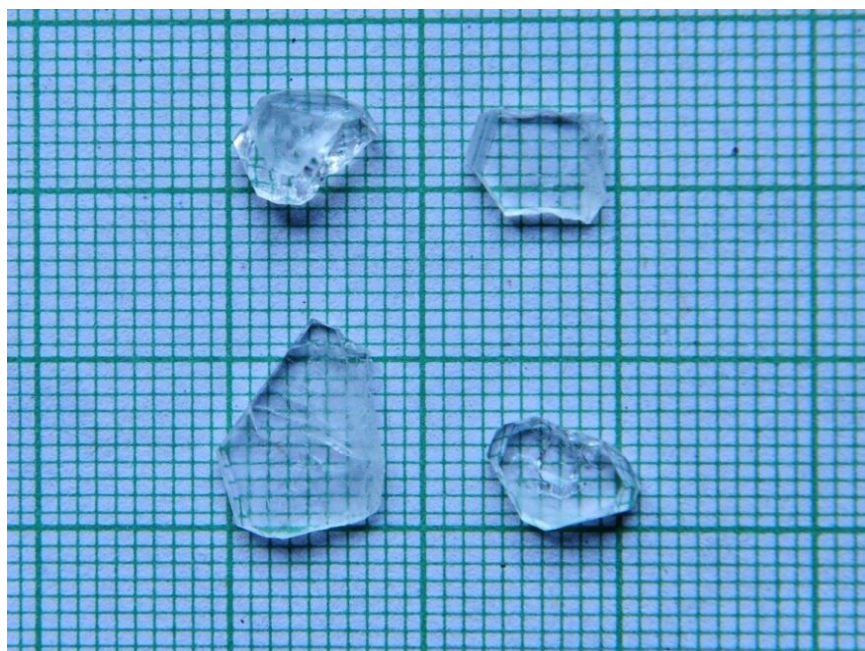

Fig. 1: Photograph of as grown crystals of BTCC

3. RESULTS AND DISCUSSION

3.1 High-resolution X-ray diffractometry study on BTCC

The crystalline perfection of the grown single crystals was characterized by HRXRD by employing a multicrystal X-ray diffractometer developed at NPL [19]. The well-collimated and monochromatedMoKα_1 beam obtained from the three monohromator Si crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,-,-,+) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B(taken as zero for the sake of convenience) starting from a suitable

arbitrary glancing angle and ending at a glancing angle after the peak so that all the meaningful scattered intensities on both sides of the peak include in the diffraction curve. The DC was recorded by the so-called ω scan wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit. Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the crystal and the possible layers which may sometimes form on the surfaces on crystals grown by solution methodsand also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferentialetchent of water and acetone mixture in 1:2 volume ratio.
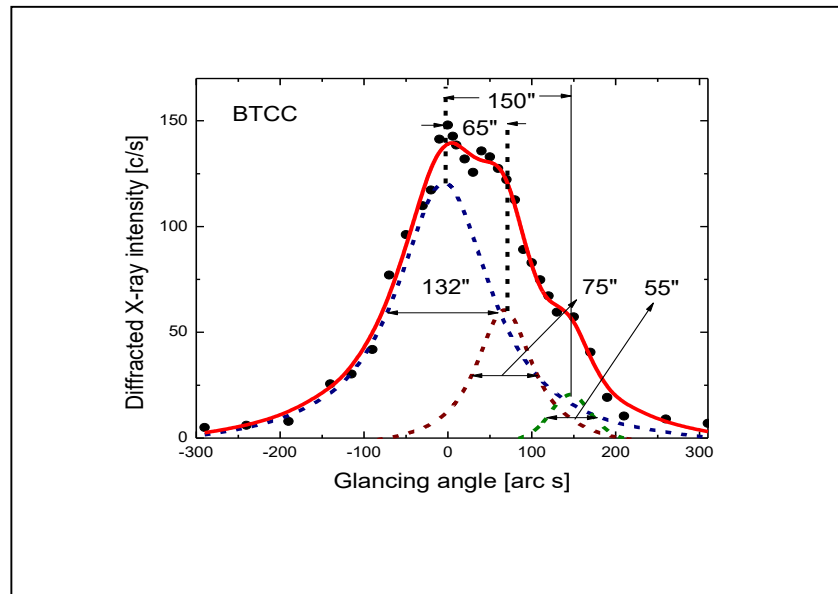
Fig. 2: HRXRD spectrum of BTCC

Fig. 2 shows the high-resolution diffraction curve (DC) recorded for a typical BTCC single crystal specimen using diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains two additional peaks, which are 65 and 150 arcs away from the main peak. These additional peaks depict internal structural low angle (tilt angle > 1 arc min but less than a degree) boundaries, whose tilt angles (misorientation angle between the two crystalline regions on both sides of the structural grain boundary) are 65 and 150 arcs from the main crystal block [20]. The FWHM (full width at half maximum) of the main peak and the low angle boundaries are respectively 132, 75 and 55 arcs. Though the specimen contains low angle boundaries, the relatively low angular spread of around 600 arcs (~ one sixth of a degree) of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good. The effect of such very low angle boundaries may not be very significant in many device applications, but for applications like phase matching, it is better to know these minute details regarding crystalline perfection. Thermal fluctuations or

mechanical disturbances during the growth process could be responsible for the observed low angle boundaries.

3.2 CHN analysis

The elemental analysis of the as grown crystals of BTCC is performed using Elemental Vario El III Elemental analyzer. The molecular components carbon, hydrogen and nitrogen of the BTCC single crystals are experimentally measured. The results of the study are given in the Table 1.

Table 1: Results of elemental (C, H and N) analysis of BTCC

Weight Composition %					
Carbon		**Hydrogen**		**Nitrogen**	
Theoretica	Experimental	Theoretical	Experimental	Theoretic	Experimental
7.16	7.17	2.40	2.39	16.69	16.71

3.3 Spectroscopic studies of BTCC

The UV visible NIR spectrum was taken in the wavelength range of 200-1100nm, using Perkin Elmer UV Win Lab and is shown in Fig.3. The UV cut-off wavelength is found to be 320 nm. There is no significant absorption in the 300-1000 nm visible range. The crystal is appeared to be a good transmitter in the visible region. Using Tauc'srelation [21] a graph has been plotted between hv and $(\alpha hv)^2$ to measure the direct band gap value, where α is absorption coefficient and hv is the energy of the incident photon. From the plot (Fig.4) the band gap of BTCC is found to be 3.75eV. BTCC crystal has large band gap compared with other prominent organometallic crystals such as ATCC [22], MMTG [23], BTCZC [24] and BTZB [25] (Table 2).

The urbachenergy is calculated by the following equation:

$$\alpha = \alpha_0 \exp(\frac{hv - E_g}{E_u})$$

Where α_o and E_g are the material parameter, 'hv' is the photon energy and E_u is the Urbachenergy [26-28].Urbach energy is determined by plotting $\ln(\alpha)$ vs. E and fitting the linear portion of the curve with a straight line (Fig.5). The Urbach energy is found to be 0.046eV.

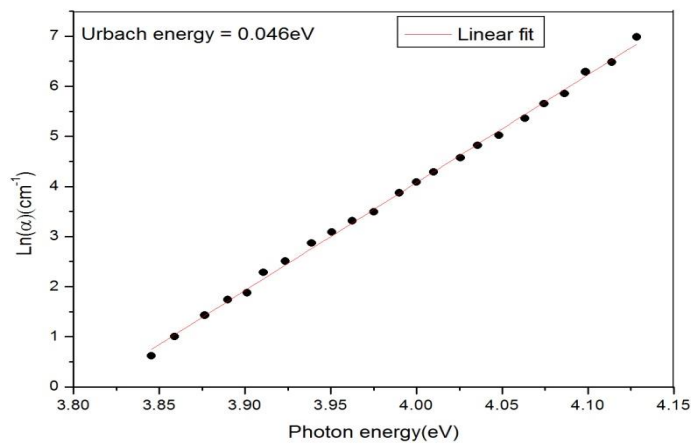**Table: 2 Direct Band gap of Organometallic compounds.**

| Sample	Direct band gap (eV)
ATCC	3.6
MMTG	3.5
BTCZC	3.65
BTZB	3.5
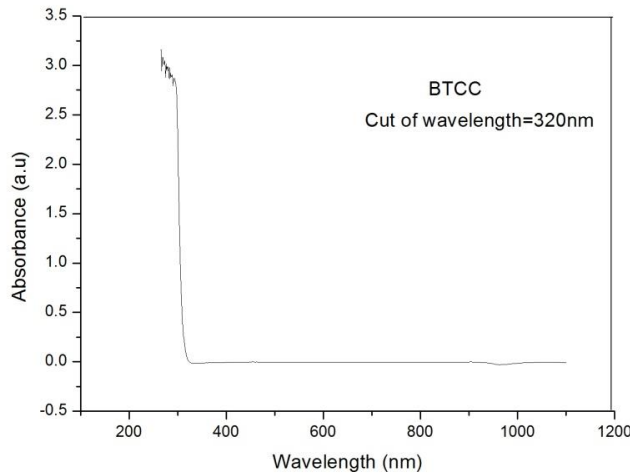
Fig. 3: UV visible NIR absorption spectrum of BTCC
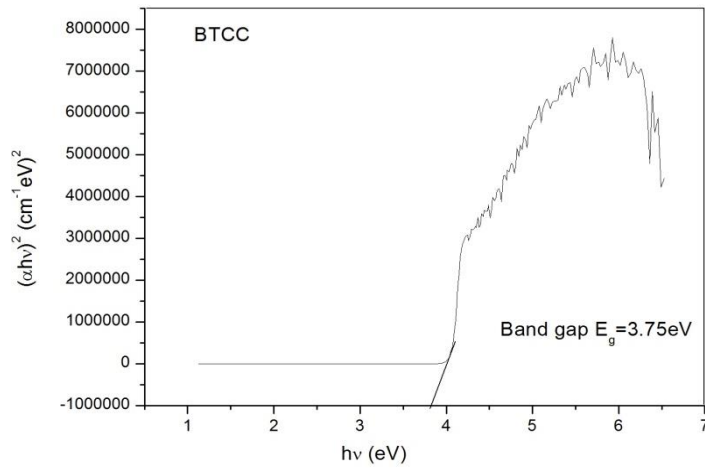
Fig.4: Tauc's plot of BTCC

Fig. 5: The dependence of ln(α) with incident photon energy

3.4 Thermal analysis of BTCC

The thermal studies (TGA/DTA) of the BTCC crystals were performed by Perkin Elmer STA6000 and is shown in Fig.6.Thermal analysis was carried out in the range 40-700^{0}C at a rate of 10^{0}C/min in inert nitrogen atmosphere. The DTA endothermic peak at 213^{0}C, coincides with the major weight loss in the TG trace. This high-temperature weight loss may be due to melting and decomposition of BTCC. The melting point of BTCC shows higher value in comparison to the endothermic peak of BTZA [29] and BTCA [30] in the same family.
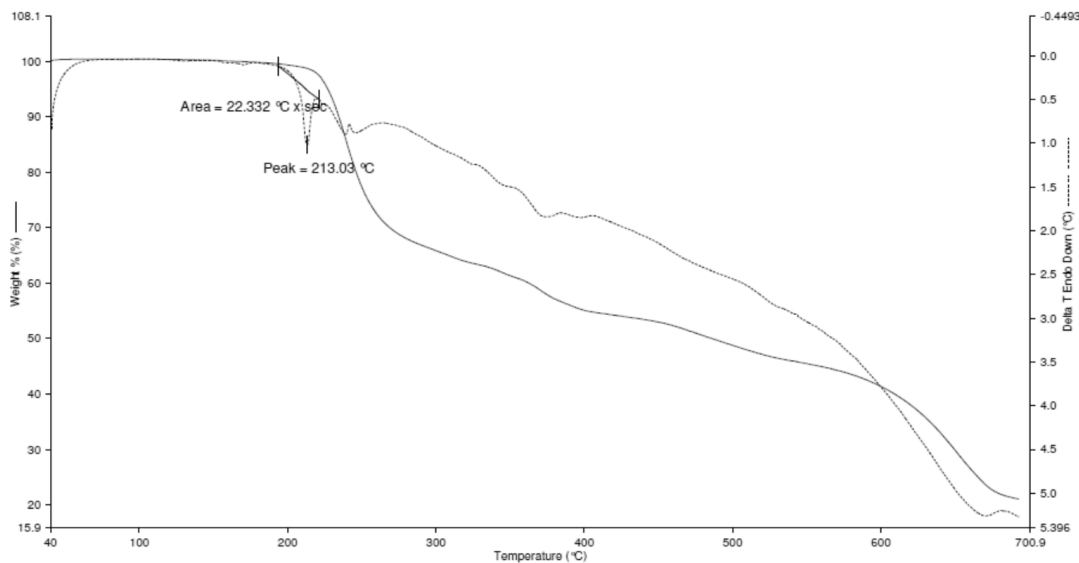
Fig. 6: TG-DTA curve of the grown BTCC crystals

3.5 Photopyroelectric (PPE) studies of BTCC

The thermal parameters of the crystals are measured using improved Photopyroelectric technique [31]. The grown selected BTCC sample is attached to apolyvinylidene difluoride (PVDF) film of thickness 28μm the pyroelectric detector. The thermal wave produced by the heating source (He-Cd laser of wavelength λ = 442 nm KIMMON, output power120mW) was allowed to propagate through the sample and are detected by the pyroelectric detector having pyroelectric coefficient =0.25×10^{-8} Vcm^{-1}K^{-1}. The Pyroelectric detector, sample and the backing medium should be thermally thick during the measurements. The intensity of the light from the laser was modulated using a mechanical chopper (SR 540). A lock-in amplifier (SR 830) was used to measure the signal output. The frequency dependence of PPE amplitude and phase for BTCC crystal is shown in Fig.7 (a) and Fig.7 (b) respectively.   The measured thermal parameters at a modulation frequency 40Hz such as Thermal effusively (e), Thermal diffusivity (α), Thermal conductivity (k), Heat capacity (C$_p$) of the BTCC crystals are given in the Table 3. It is found that thermal effusivity, thermal conductivity and specific heat capacity of the selected BTCC sample is slightly higher than that of the BTZC crystals in the same family [32].
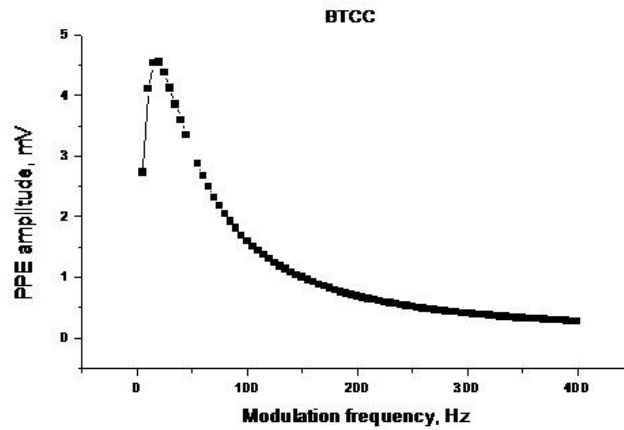
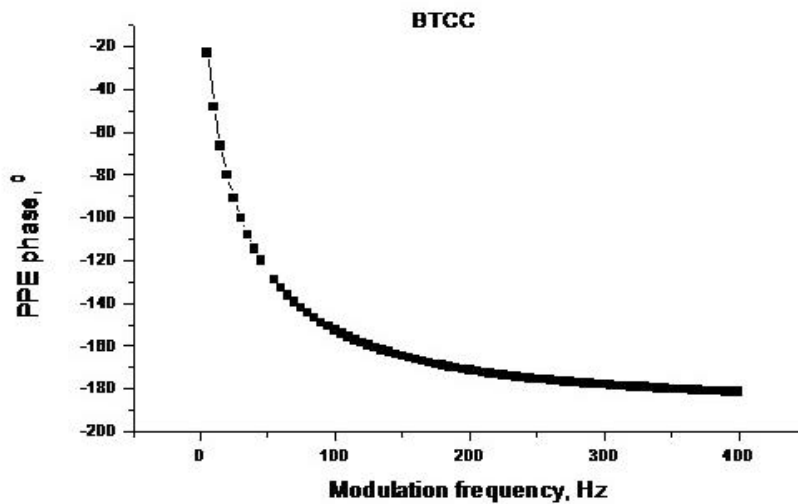**Fig. 7 (a):   Frequency dependence of PPE amplitude**

**Fig. 7 (b): Frequency dependence of PPE phase**

Table 3: PPE measurements of BTCC

Sample Thickness (mm)	Modulation Frequency (Hz)	Thermal effusivity E (Ws½/m²K)	Thermal diffusivity α (×10⁻⁶m²/s)	Thermal conductivity k (W/mK)	Sp. Heat capacity Cp (J/kgK)
1.6	40	3283	6.31	8.24	713

**3.6 Dielectric properties of BTCC**

The dielectric study of a crystal reveals the interaction of the molecules in the presence of an external electric field. When an electric field oscillates, the dipole in the system tend to follow the field and experiences some friction due to its collision with other molecule in the system or some energy is absorbed from the field, which is known as the dielectric loss. The dielectric studies are measured from the Agillent E4980 LCR meter, and plotted with frequency in the range 100Hz to 100kHz in the temperature range 25^0C– 145 ^{0}C with an interval of 20^0 C. The graph of dielectric loss (Fig.8)

shows an exponential decrease at high frequencies. The very low dielectric loss at higher frequencies is an indication of the perfection and purity of the crystal sample. The dielectric loss increases with temperature indicating high energy absorption. The real part of the dielectric constant is plotted in the temperature range 25^0-165^0C (Fig.9). At low frequencies all kinds of polarization are well active and the space charge polarization are absent at higher frequencies. Hence the BTCC sample exhibits high dielectric constant at high temperature. The space charge polarization is trusted on purity and perfection of the crystals [33, 34]. Dielectric studies of sample indicate the strong S.H.G conversion efficiency with lesser defects of the given crystals [35]. The dielectric constant and dielectric loss plotted against temperature for different frequencies is shown in Fig.10 and Fig.11 respectively. Both the dielectric constant and dielectric loss having very high value at low frequencies increase with increasing temperature.
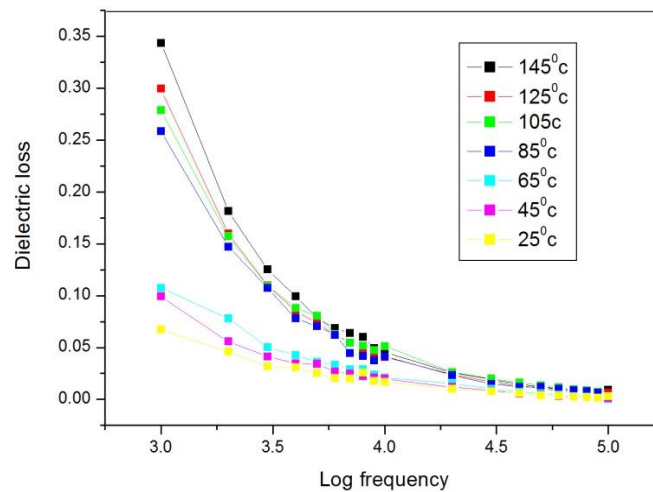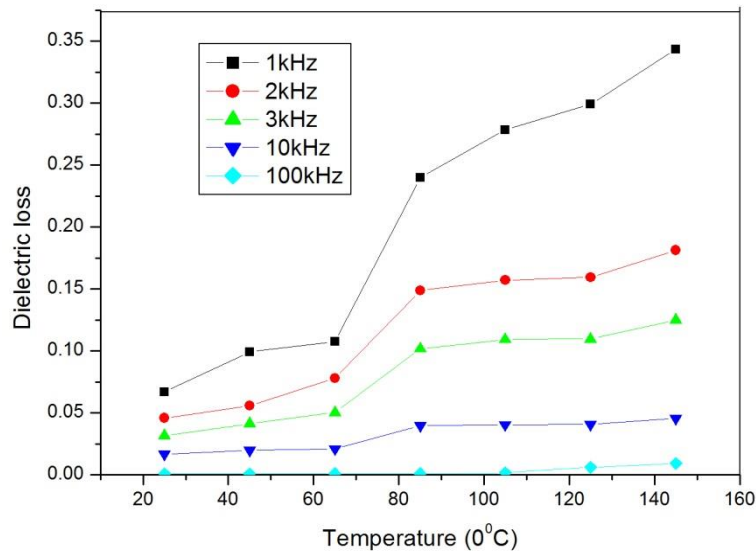

Fig.8: Dielectric loss versus log frequency
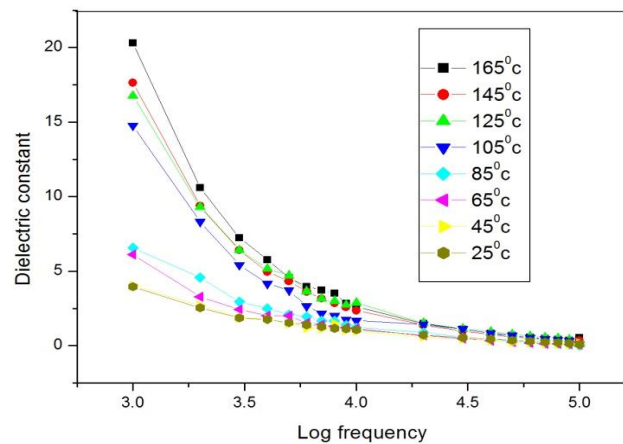
**Fig.9: Dielectric constant versus log frequency**
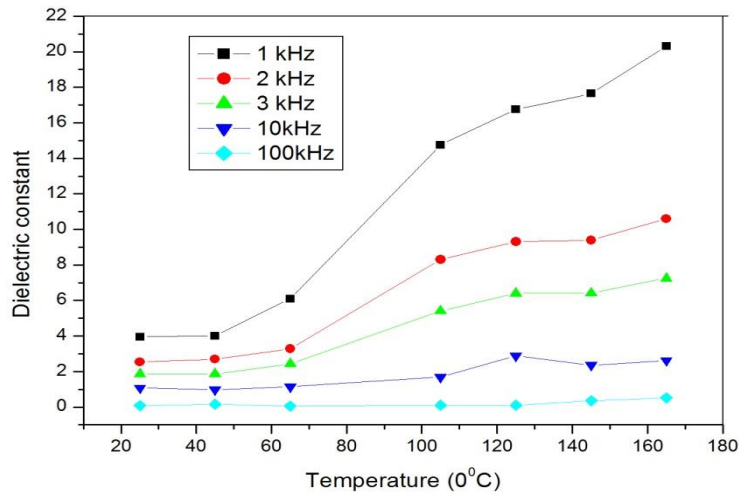
**Fig.10: Dielectric constant versus Temperature for different frequencies**

Fig. 11: Dielectric loss versus Temperature for different frequencies

3.7 A.C. Conductivity studies of BTCC

The ac electrical conductivity studies of the grown BTCC crystals were also done with the above Agillent E 4980 LCR meter. The graph of logarithmic conductivity with logarithmic frequency for the temperature range 130-180^{0}C is plotted having a positive slope and is found to increase with frequency, at all temperatures (Fig.12). The Arrhenius plot (log σ_{ac}T versus 1000/T) reveals that the sample exhibits Arrhenius type conductivity behavior as shown in Fig.13.The slope of the Arrhenius plot reveals that the activation energy of the crystal is 0.19eV under the temperature of investigation.
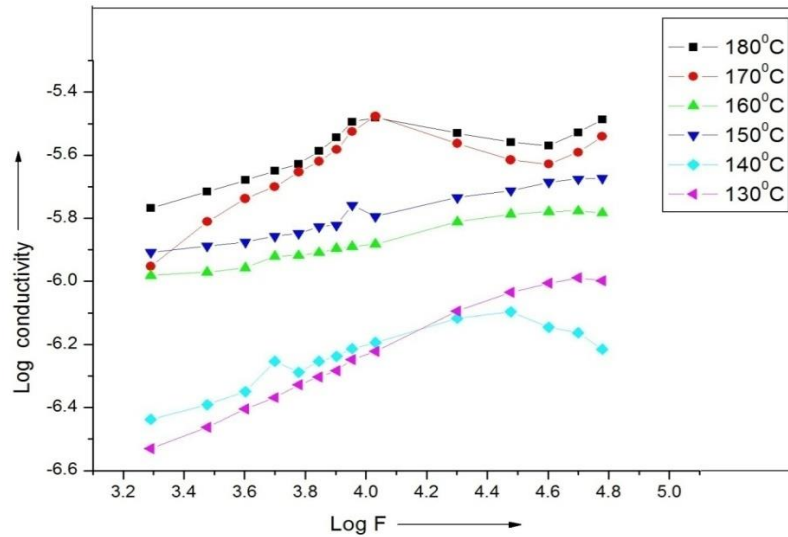
**Fig.12: log conductivity versus log frequency for various temperatures**
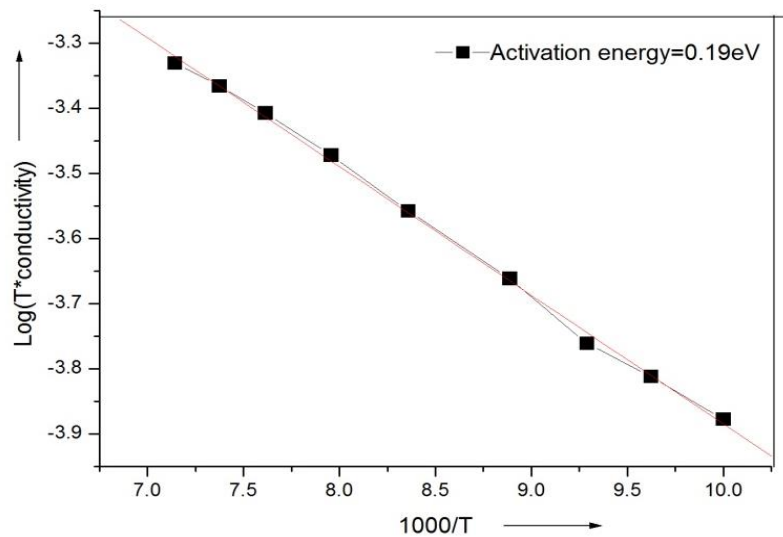
Fig.13: Arrhenius plot of BTCC

3.8 Piezoelectric studies of BTCC

Piezoelectricity is the phenomenon in which electric charges are separated when the material is subjected to an external stress. The inverse effect is also possible – that an applied field can produce vibration in the crystal. The crystal having non-centrosymmetric structure can exhibit piezoelectric properties. In the absence of external stress, the internal electric field is zero because of the symmetric charge distribution at their lattice sites. But when the crystal is under stress, the charges are displaced and the electric field is developed. The materials showing this phenomenon are known as piezoelectric materials. The common application of piezoelectric materials is in transducers and in delay lines. A good piece of the crystal with area 30 mm^2 and thickness 1.50 mm was prepared, and is placed in the piezometer system. Piezoelectric charge coefficient (d_{33}pC/N) was calculated with a piezometer system in the tapping frequency range of 50-300Hz and applying a tapping force

of 0.25N at room temperature and the obtained value is 8pC/N. The P E loop (Fig.14) of the BTCC crystal was taken using computer controlled P-E loop tracer. For an applied field of 40.4 kV/cm polarization reaches saturation (P_{max}=0.637µC/cm^2). Also it is measured that polarization has a value around 0.346µC/cm^2 at near zero electric field (remnant polarization, P_r) and the coercive filed, is 21.17kV/cm. A corona dc poling technique is employed to the shaped BTCC crystal, but also after poling the hysteresis loop parameters remains unaffected as an indication of saturation of dipoles. The loop parameters are tabulated in the Table 4.
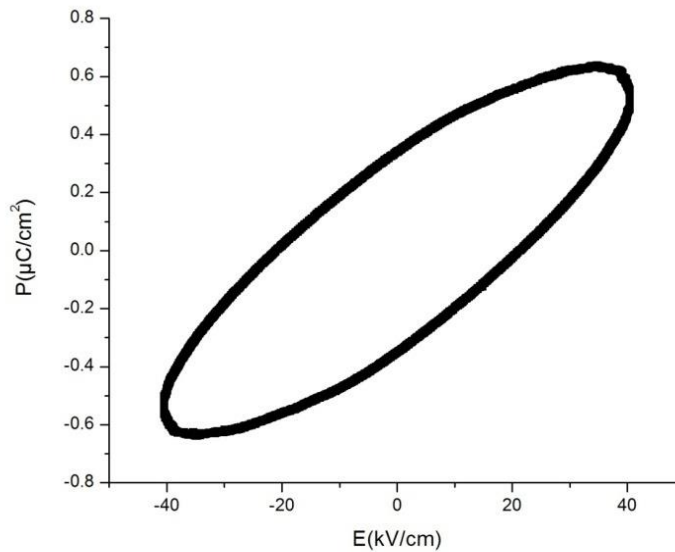

Fig.14: P-E loop of BTCC

Table 4: Hysteresis loop parameters of BTCC crystal

Sample	Thickness of the sample (mm)	Remnant polarization (P_r) (µC/cm^2)	Coercive field (E_c) (kV/cm)	Maximum Electric field E_{max} (kV/cm)	Maximum Polarization P_{max} (µC/cm^2)
BTCC (Unpoled)		0.346	21.174	40.402	0.637
BTCC (Poled)	1.5	0.346	21.174	40.402	0.637

3.9 Photoconductivity studies of BTCC

The photoconductivity measurement of the BTCC samples has been carried out using the Keithley 6485 Pico ammeter. The dark current was recorded by keeping the sample unexposed to any radiation. The applied field was varied from 0 to 400 V/cm at room temperature (305K). The sample was illuminated with a mercury lamp of 80W power by focusing a spot of light to the sample with

the help of a converging lens. The photo current was measured by varying the applied field for the same range in step of 20V. The variations of photo current (I_p) and dark current (I_d) with applied field is shown in the Fig.15. The dark current is always higher than the photocurrent for different applied field which is said to exhibit negative photoconductivity. The negative photoconductivity exhibited by the sample may be due to the reduction in the number of charge carriers or their life time, which is explained by Stockman model [36].
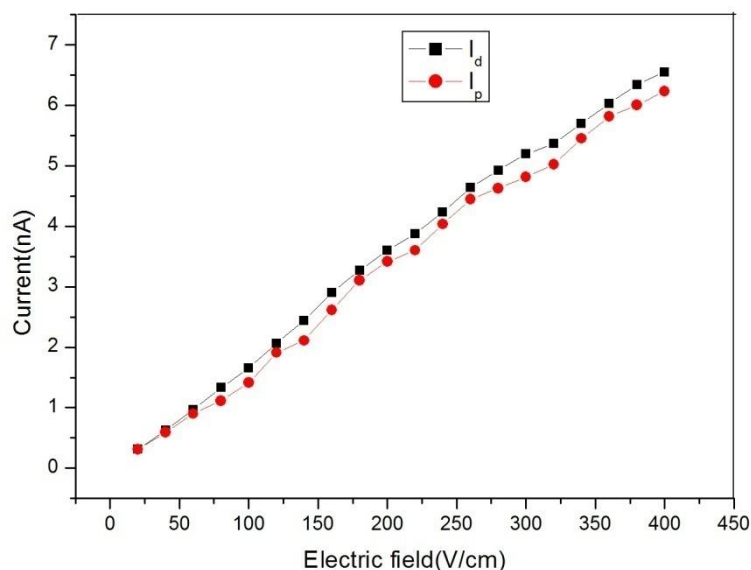
Fig.15: Field dependent conductivity of BTCC crystals

4. CONCLUSION

Single crystals of Bisthiourea cadmium chloride (BTCC) were prepared using slow evaporation technique. The crystalline perfection of the sample was estimated through high resolution X- ray diffraction technique. The UV cut-off wavelength and optical band gap were calculated from optical absorption studies. The dielectric loss and dielectric constant were measured from the Agillent E4980 LCR meter. The conductivity studies were carried out and the Arrhenius type behavior is revealed. Photopyroelectric studies of the crystals were done and thermal parameters of the BTCC crystals were measured. Piezoelectric studies were conducted and the Hysteresis loop parameters are measured from the PE loop. The field dependence of conductivity of the BTCC sample was measured from the photoconductivity studies.

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CONFLICT OF INTEREST

Authors declare no conflict of interest.

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