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# Optical, crystalline perfection and mechanical studies on unidirectional grown bis(thiourea) cadmium zinc chloride single crystal

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ABSTRACT

Optically transparent and bulk single crystal of bis(thiourea) cadmium zinc chloride was successfully grown by unidirectional crystal growth technique. The quality of the crystal was examined by high-resolution X-ray diffraction analysis. The cell parameters and the crystallinity of the grown crystal were estimated by the single-crystal and powder X-ray diffraction analyses, respectively. Optical transmittance of the crystal was recorded using the UV–vis–NIR spectrophotometer. The optical band gap and optical constant of the material were calculated by using transmission spectrum. Microhardness measurements were made for the grown crystal using Vicker's microhardness tester. The dielectric loss and dielectric constant measurements as a function of frequency and temperature were measured for the grown crystal.



## 1. Introduction

Materials with excellent optical nonlinearities have been studied extensively for their possible applications in optoelectronics and laser industries [1,2]. Although inorganic compounds exhibit relatively low second order susceptibility and restricted birefringence, it is possible to grow them as good quality large single crystals. The demand for compounds having large nonlinear optical coefficients led to the discovery of a very large number of organic compounds. Organic compounds are often formed by weak hydrogen and Van der Waal bonds and, hence, possess a high degree of charge delocalization leading to large NLO coefficients [3]. However, organic compounds frequently suffer from volatility, poor thermal stability, poor mechanical strength and undesirable growth habit, making them unattractive for device fabrication. In order to overcome these difficulties, semi-organic materials have been proposed in which the high optical nonlinearity of a purely organic compound is combined with the favorable mechanical and thermal properties of inorganics [4]. Among the semi-organic nonlinear optical materials, metal complexes of thiourea have received much attention because they can be used as better alternatives for KDP crystals in frequency doubling and laser fusion experiments [5,6]. Thiourea molecules also possess a large dipole moment and have the ability to form an extensive network of hydrogen bonds, which proves that thiourea molecules can be used as inorganic matrix modifier [7,8]. Bis(thiourea) cadmium zinc chloride, hereafter referred to as BTCZC, is a semi organic nonlinear optical crystal, which has an excellent figure of merit [9]. In the past decades, many efforts have been made to improve the crystal quality and growth rate to meet the requirements of inertial confinement optical fusion [10]. The unidirectional growth method has been introduced for the growth of bulk single crystals from solution [11]. Crystals grown by this technique are reported to have better optical qualities than the conventionally grown crystals. The features include avoiding microbial growth, maximum solute–crystal conversion efficiency and visualization of growth rate precisely for individual faces [12–14]. Moreover, Dinakaran et al. have reported that this technique also offers the benefit of growing a crystal along a specific orientation instead of natural facets [15]. The present investigation is aimed at the growth of bulk BTCZC single crystal by unidirectional method with a slight modification in the growth apparatus. The grown crystal has been subjected to high resolution X-ray diffraction analysis, powder XRD studies, UV–vis transmission spectral analysis, optical band gap measurements, Vicker's hardness test and dielectric studies.

## 2. Experimental

### 2.1. Synthesis of material

The title compound was synthesized from purified thiourea, cadmium chloride and zinc chloride in the stoichiometric ratio 2:1:1, and the chemical reaction is

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**Fig. 1.** Photograph of unidirectional grown single crystal.

given as

$$2[NH_2CSNH_2] + CdCl_2 + ZnCl_2 \rightarrow ZnCd[NH_2CSNH_2]_2[Cl_2]_2 \quad (1)$$

The synthesized material was further purified by re-crystallization process using de-ionized water as solvent, stirred continuously resulting in a homogeneous solution, and kept inside the constant temperature bath to obtain seed crystals by spontaneous nucleation. Seed crystal, which is free from defects, was selected and mounted in the ampoule maintained to grow a large single crystal. The product was purified by repeated re-crystallization before it was used for crystal growth runs.

### 2.2. Growth assembly and crystal growth

The growth setup used here is a modified version of the Sankaranarayanan–Ramasamy (SR) method, which is somewhat similar to our earlier, reported one [16]. The assembly was optimized in such a way as to obtain a maximum temperature profile at the top. A seed was fixed at the bottom of the ampoule and filled with the saturated solution of bis(thiourea) cadmium zinc chloride, which was mounted along the axis of the inner cylinder. The ampoule was designed with an inner L-bend, which controls spontaneous nucleation on the top wall of the ampoule and prevents poly crystallization as well as microbial growth. The temperature gradient creates a concentration gradient along the growth ampoule, having a maximum super saturation at the bottom of the ampoule and a minimum at the top of the ampoule, thereby avoiding any possibility of a spurious nucleation along the length of the ampoule. The excess solute generated by evaporation of the solution is driven down the ampoule by the temperature gradient of the setup. Thus, the growth was initiated from the seed fixed at the bottom of the ampoule along the preferred orientation. The growth rate of the crystal was found to be 4 mm per day. The bulk single crystal of 95 mm length and 12 mm diameter has been grown successfully within a period of 24 days. The photograph of the grown crystal is shown in Fig. 1.

## 3. Results and discussion

### 3.1. High-resolution X-ray diffraction analysis

The crystalline perfection of the grown single crystal was characterized by HRXRD by employing a multi crystal X-ray diffractometer developed at NPL [17]. The well-collimated and monochromated MoK$\alpha_1$ beam obtained from the three monochromator 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 a minimum angular interval of 0.4 arc s. The DC was recorded by the so-called $\omega$ scan, wherein the detector was kept at the same angular position $2\theta_B$ with a wide opening for its slit. Fig. 2 shows the high-resolution diffraction curve (DC) recorded for the grown BTCZC single crystal using (1 1 0) diffracting planes in symmetrical Bragg geometry by employing the multi crystal X-ray diffractometer with MoK$\alpha_1$ radiation. As seen in the figure, the DC contains a single sharp peak, and indicates that

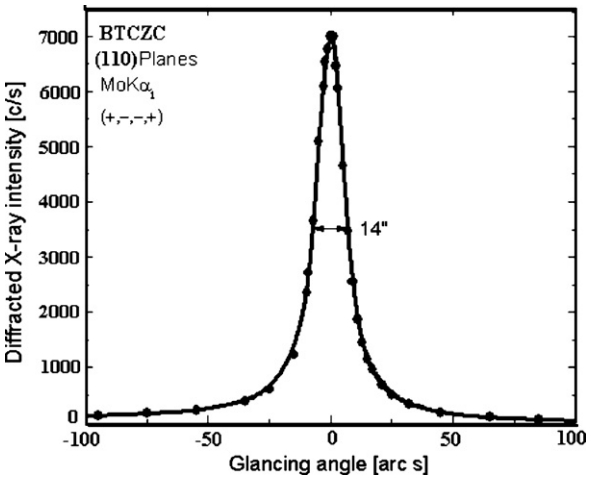


**Fig. 2.** High resolution X-ray diffraction spectrum of BTCZC single crystal.

the specimen is free from structural grain boundaries. The FWHM (full width at half maximum) of the curve is 14 arc s, which is very close to that expected from the plane wave theory of dynamical X-ray diffraction [18], for an ideally perfect crystal. As the crystal is free from structural grain boundaries and the FWHM is only 14 arc s, the grown crystals are very much suitable for the device fabrication.

### 3.2. Single crystal X-ray diffraction studies

To determine the unit cell parameters, the grown crystal was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 automatic X-ray diffractometer with an incident MoK$\alpha$ radiation ($\lambda$ = 0.71703 Å). The X-ray analysis reveals that the grown crystal belongs to orthorhombic system with space group $P2_12_12_1$ unit cell parameters $a$ = 11.918(5) Å, $b$ = 6.821(8) Å and $c$ = 13.114(6) Å and is well-matched with the reported literature [9].

### 3.3. Powder X-ray diffraction studies

Powder X-ray diffraction pattern was recorded using a Rich Seifert diffractometer with Cu K$\alpha$ ($\lambda$ = 1.5418 Å) radiation by crushing the BTCZC crystal into fine powder. The sample was scanned over the range 10–70° at a rate of 2° per min. The indexed powder XRD pattern of the grown crystal is shown in Fig. 3. The diffraction

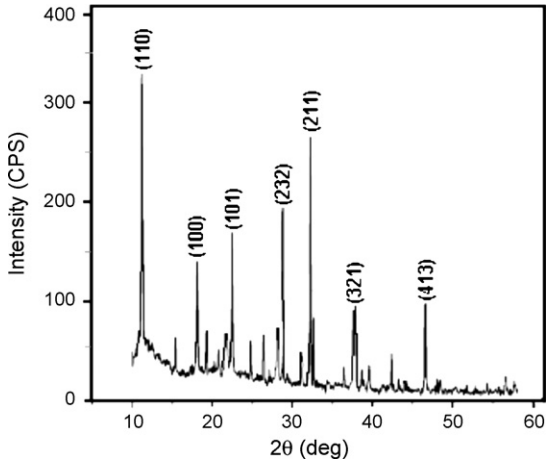


**Fig. 3.** Powder XRD pattern of BTCZC single crystal.

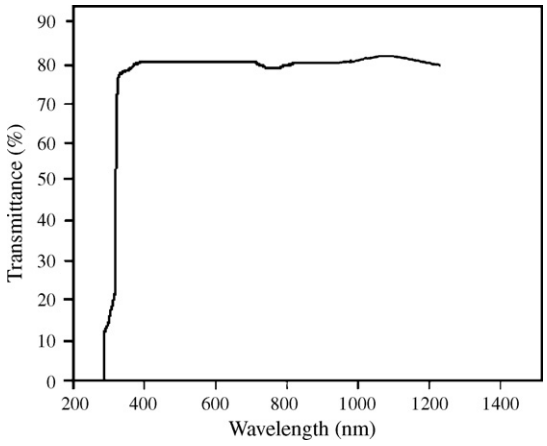


**Fig. 4.** UV-transmittance spectrum of grown BTCZC single crystal.

patterns have been indexed by the least square fit method, which confirms the perfection of good quality single crystal. The peak corresponding to (1 1 0) has the maximum intensity of 345 counts per second. The cell parameter values coincide with single crystal XRD results.

### 3.4. Optical transmission spectral analysis

The optical transmission spectrum (Fig. 4) was recorded for the grown crystal of thickness 2 mm using Varian Cary-5E UV–vis-NIR spectrometer in the range of 200–1600 nm. From the transmission spectrum, it is observed that the crystal possesses more than 80% transmission in the entire visible and near infrared region with the lower cut-off wavelength at 250 nm. In the longer wavelength region (380–1300 nm), the crystal is observed to be highly transparent. The absence of absorption in this region shows that this crystal could be used for optical applications. The optical absorption co-efficient ($\alpha$) was calculated using the following relation,

$$a = \frac{1}{t}\log\frac{1}{T} \tag{2}$$

where $T$ is the transmittance and $t$ is the thickness of the crystal.

As direct band gap, the crystal under study has absorption co-efficient ($\alpha$) obeying the following relation for high photon energies ($h\nu$),

$$a = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{3}$$

where $E_g$ is band gap and $A$ is constant. The graph between $(\alpha h\nu)^2$ and $(h\nu)$ is shown in Fig. 5 and it gives the band gap of the crystal

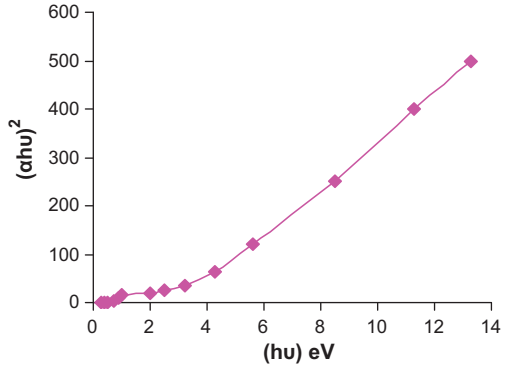


**Fig. 5.** Plot of $\alpha$ vs photon energy of the title crystal.

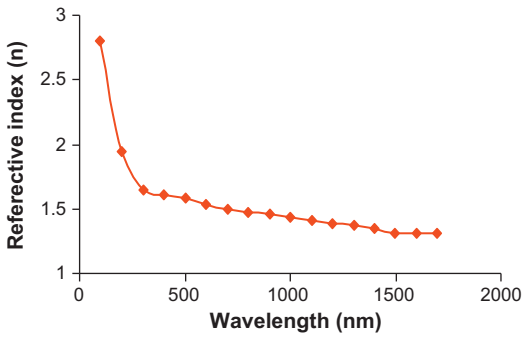


**Fig. 6.** Variation of refractive index with wavelength.

as 3.65 eV. As a consequence of wide band gap, the grown crystal has large transmittance in the entire visible region [19].

### 3.5. Determination of optical constant

The dependence of optical absorption co-efficient with photon energy helps to study the band structure and the type of transition of the electron. The absorption coefficient ($\alpha$) and the optical constant ($n$, $k$) are determined from the transmission ($T$) and reflection ($R$) spectrum based on the following relations, [20,21]

$$T = \frac{(1-R)^2\,\exp(-at)}{1-R(-2at)} \tag{4}$$

The reflectance in terms of absorption coefficient can be calculated using the following relation [22]

$$R = 1 \pm \frac{\sqrt{1-\exp(-at)+\exp(at)}}{1+\exp(-at)} \tag{5}$$

and from the above equation the refractive index $n$, can be derived as

$$n = \frac{-(R+1\pm\sqrt{-3R^2+10R-3})}{2(R-1)} \tag{6}$$

The dependence of refractive index ($n$) on wavelength is shown in Fig. 6.

### 3.6. Mechanical studies

Hardness of a material is the measure of resistance it offers to local deformation, which is an extremely important parameter for the fabrication of devices. The cut and well polished crystal was subjected to static indentation tests at room temperature using Vicker's microhardness tester. Indentations were made on the sample plane with the load ranging from 25 to 200 g, keeping the time of indentation constant at 10 s for all trials. The distance between the consecutive indentations was kept more than five times the diagonal length of the indentation to avoid surface effects. The Vicker's hardness (Hv) numbers at different loads were calculated [23] using the following relation

$$\mathrm{Hv} = 1.8544\frac{p}{d^2}(\mathrm{kg/mm^2}) \tag{7}$$

where, '$P$' is the applied load in kilograms and '$d$' is the average diagonal length of the indentation marks in millimeter and the result is plotted (Fig. 7). The grown crystal exhibits the reverse indentation size effect (RISE), in which the hardness value increases with the increasing load [24,25]. The work hardening co-efficient ($n$) was calculated to be 2.104. Samples exhibit the formation of cracks around at 100 g due to the release of internal stress generated

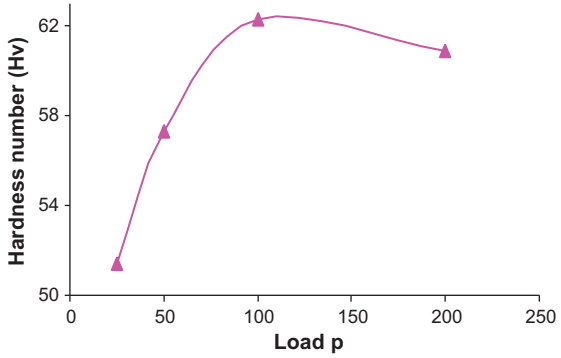


**Fig. 7.** Plot of $P$ vs Hv for BTCZC crystal.

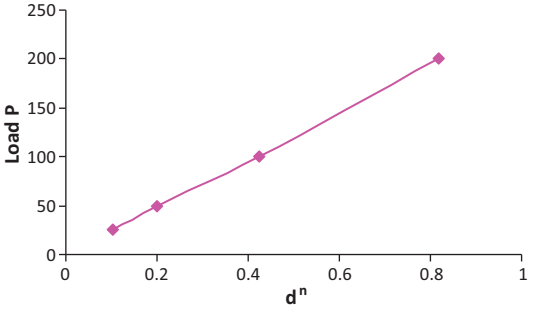


**Fig. 8.** Plot of $\log p$ vs $\log d$ for BTCZC crystal.

locally by indentation. According to Meyer's law,

$$p = k_1 d^n \tag{8}$$

where $k_1$ is the standard hardness found out from the $p$ vs $d^n$ graph (Fig. 8). It is known that the material takes some time to revert to elastic mode after the applied load is removed, so a correction $x$ is applied to the observed $d$ value. Meyer's law may be modified as,

$$p = k_2(d + x)^2 \tag{9}$$

Simplifying Eqs. (8) and (9), we get

$$d^{n/2} = \left(\frac{k_2}{k_1}\right)^{1/2} d + \left(\frac{k_2}{k_1}\right)^{1/2} x \tag{10}$$

The slope of $d^{n/2}$ vs $d$ (Fig. 9) yields $(k_2/k_1)^{1/2}$ and the intercept is a measure of $x$. From the hardness value, the yield strength ($\sigma_v$)

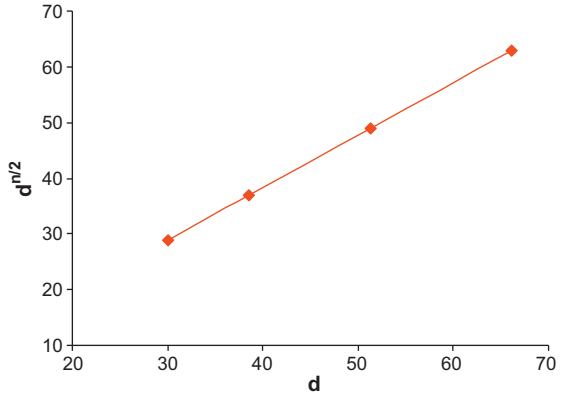


**Fig. 9.** Plot of $d^{n/2}$ vs $d$ for BTCZC crystal.

**Table 1**
Hardness data for unidirectional grown BTCZC.

| Crystal | $n$ | $k1$ (kg/mm$^2$) | $k2$ (kg/mm$^2$) | $x$ (μm) | $\sigma_v$ (MPa) |
|---|---|---|---|---|---|
| BTCZC | 2.104 | 110 | 7.2453 | 18.664 | 165.30 |

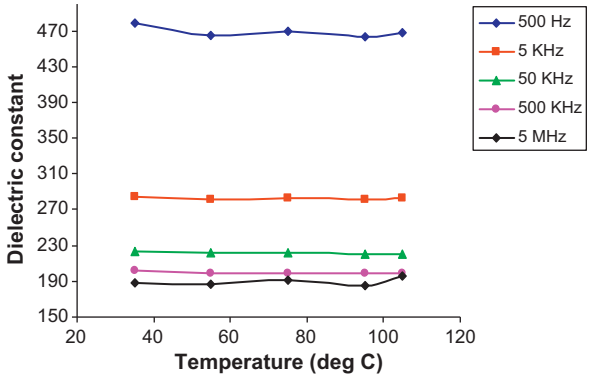


**Fig. 10.** Variation of dielectric constant with $\log f$.

can be calculated using the relation [26,27]

$$\sigma_v = \frac{Hv}{2.9}\left[(1-(n-2)) \times \left\{\frac{12.5(n-2)}{1-(n-2)}\right\}^{n-2}\right] \tag{11}$$

The calculated yield strength is equal to 165.30 MPa for BTCZC single crystal. The hardness parameters are listed in Table 1.

### 3.7. Dielectric studies

The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. Hence, the grown crystal was subjected to dielectric studies using a HIOKI HITESTER model 3532-50 LCR meter in the frequency range from 500 Hz to 5 MHz for different temperatures. The surface of the sample was electroded with silver paste for electrical contact. The dielectric constant and dielectric loss have been calculated using Eqs. (12) and (13)

$$\varepsilon = \frac{cd}{A\varepsilon_0} \tag{12}$$

$$\varepsilon' = \varepsilon \tan \partial \tag{13}$$

where $d$ is the thickness of the sample; $A$ is the area of the sample. Dielectric constant and dielectric loss measurements of BTCZC crystal are shown in Figs. 10 and 11. From the plots, it is observed that the dielectric constant and dielectric loss decrease with increase in frequency and attains saturation at higher frequencies. The very high values of dielectric constant at low frequencies may be due

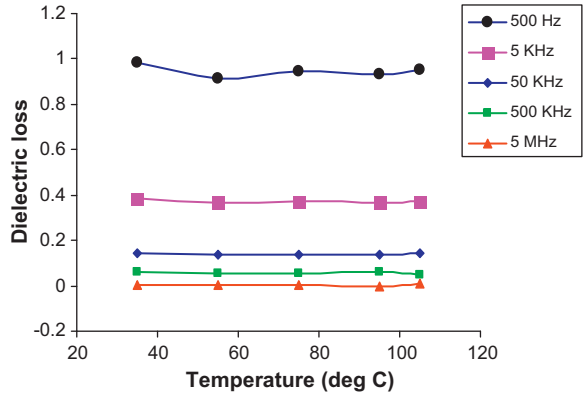


**Fig. 11.** Variation of dielectric loss with $\log f$.

to the presence of all the four polarizations, namely, space charge, orientational, ionic and electronic polarizations and its low value at high frequencies may be due to the loss of significance of these polarizations gradually [28]. The low value of dielectric loss at high frequencies reveals the high optical quality of the crystal with lesser defects [29], which is the desirable property for optical applications.

## 4. Conclusions

Bulk single crystal of semi-organic bis(thiourea) cadmium zinc chloride was grown from aqueous solution by a directional solidification technique. The title material belongs to orthorhombic crystal system with space group $P2_12_12_1$. The high-resolution XRD measurements substantiate the excellent quality of the crystal free from major defects like structural grain boundaries and inclusions. The optical transmission analysis indicates that BTCZC has a wide transparency window in the entire visible and near IR regions with a lower cutoff wavelength at 250 nm. The band gap was estimated to be 3.65 eV. The micro hardness observations showed that hardness increases with increase of load, which confirms the reverse indentation size effects of the crystal. Several hardness parameters have been calculated for the grown crystal. The dielectric studies reveal that BTCZC has low dielectric constant with fewer defects, and hence this crystal can be used as a potential material for optical applications.

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