



# Band tailing in tellurium excess CdTe crystals grown from vapour phase

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**Abstract.** Absorption spectra of hexagonally structured, tellurium excess p-type cadmium telluride (CdTe) grown from vapour phase having conductivity  $2.529 \times 10^4 (\Omega \text{ cm})^{-1}$  was studied in the range 700–880 nm. The existence of phonon-assisted indirect transition was confirmed. The direct and indirect bandgaps and the involved phonon energy were identified. The analysis revealed a band tailing and the presence of a strong internal electric field responsible for the tunnelling of charge carriers.

**Keywords.** Physical vapour transport growth; cadmium telluride; spectral analysis; energy bandgap and phonon energy; band tailing; carrier tunnelling.

## 1. Introduction

Cadmium telluride has emerged as a promising material, enabling a switch over from the dependency on non-renewable energy sources, thereby slashing greenhouse gas emissions [1]. A large area CdTe diode detector with a good energy resolution and high homogeneity suitable for hard X-ray and  $\gamma$ -ray space applications was reported by Nakazawa *et al* [2]. Also, Kang *et al* [3] mooted a viable large area thin-film CdTe structure suitable for medical imaging used in radiation therapy. Thuy *et al* [4] reported on the preparation of CdTe quantum dots in aqueous phase with a potential life science application in bio-medical fluorescence labelling and could work as pH-sensitive detector for the avian influenza virus subtype A/H5N1. Zhang *et al* [5] highlighted on the viable utility of chlorine-capped CdTe as an ultrasensitive photodetector. At present, CdTe is foreseen as a potential candidate for the next-generation high-efficiency multi-junction solar cells for large-scale space PV solar energy applications [6]. Gutierrez *et al* [7] presented CdTe heterostructure-based ultra-thin solar cells enhancing the photovoltaic parameters. Efforts for yielding better energy conversion efficiency of CdTe-based photovoltaic cells were presented by Ojo and Dharmadasa [8] and Wang *et al* [9].

In the present work, we analysed the absorption spectra of CdTe crystals with hexagonal structure, a unique phase in bulk form, grown from vapour phase. The influence of excess tellurium (Te) in the grown off-stoichiometric CdTe on the optoelectronic properties of the material was probed.

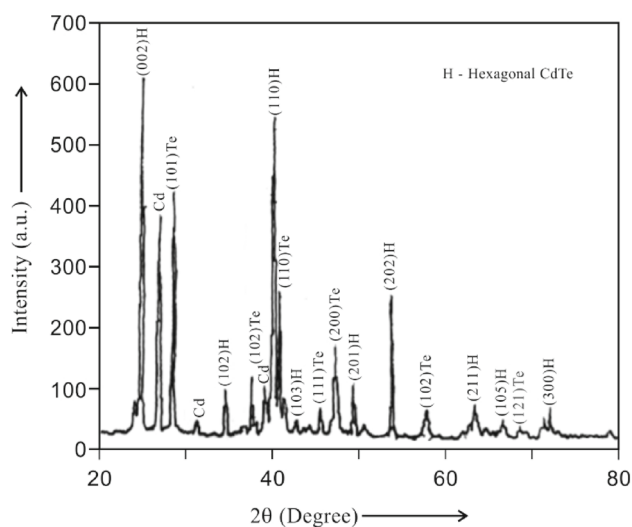
Estimation of direct and indirect bandgap energies of the grown samples was carried out. Band edge deformation due to the presence of any internal electric field and the formation of tail states was pondered.

## 2. Growth and physical properties of direct vapour transport grown cadmium telluride

An attempt to grow cadmium telluride by direct vapour transport method was carried out, which is rather an unconventional approach for this material [10], as travelling heater method (THM) [11–14] or Bridgman method [15–19] is traditionally adopted for the growth. A thoroughly cleaned quartz ampoule was loaded with the stoichiometric mixture of Cd and Te without any transporting agents [20]. The ampoule was loaded in a two-zone furnace after evacuating to a pressure of  $10^{-5}$  Torr and sealing. Initially, the temperatures of the growth and source zones were raised to 1253 K at a rate of  $5 \text{ K h}^{-1}$  using temperature controllers ensuring temperature stability within  $\pm 1 \text{ K}$  precision. After 24 h, the growth zone temperature was lowered down to 1203 K at a rate of  $5 \text{ K h}^{-1}$  setting a temperature difference of 50 K between the two temperature zones. The final source and growth zone temperatures at 1253 and 1203 K, respectively, were maintained for about 168 h. Later, both the zones were slowly cooled down to room temperature initially at a rate of  $5 \text{ K h}^{-1}$  till 673 K and thereafter at the rate of  $10 \text{ K h}^{-1}$ .

The structure of the grown CdTe crystals was probed by X-ray diffraction. The thermodynamically stable bulk form of CdTe is the cubic zinc-blende structure [21–24] because of high temperature nucleation and growth. There were reports of hexagonal wurtzite structure often found in nano CdTe crystals [25–29]. Doped thin film forms of CdTe with hexagonal structure [30–37] were synthesized by investigators in an effort to increase the efficiency of CdTe/CdS solar cell by growing the two layers with the same phase as CdSe, which possesses hexagonal phase leading to lattice matching at the interface, where the synthesis by various methods is through molecular level configuration in one way or the other. The formation of hexagonal CdTe crystal in bulk form by the physical vapour transport method adopted in the present study was confirmed from the XRD pattern in figure 1. The hexagonal structure could be due to the vapour phase nucleation and growth process analogous to thin film growth approach. Signatures of excess Te and nonreacted Cd material within the lattice of the material was also observed in the XRD pattern. The differential vapour pressure imbalances would be influencing the mass transfer during growth process attributing to the off-stoichiometric feature of the CdTe crystals [10].

The grown CdTe crystals exhibited p-type conductivity, an indication of excess Te presence [38,39], with atomic composition percentage of Cd and Te as 42.53 and 57.47, respectively, which was confirmed by the energy dispersion analysis of X-rays (EDX). The agglomeration of tellurium [16,40–44] contributed to the observed off-stoichiometry of the grown sample. The carrier concentration and conductivity, confirmed from Hall effect measurement for the grown CdTe at room temperature, were found to be  $1.425 \times 10^{16} \text{ cm}^{-3}$  and  $2.529 \times 10^4 (\Omega \text{ cm})^{-1}$ , respectively.



**Figure 1.** X-ray diffractogram of the vapour phase grown CdTe.

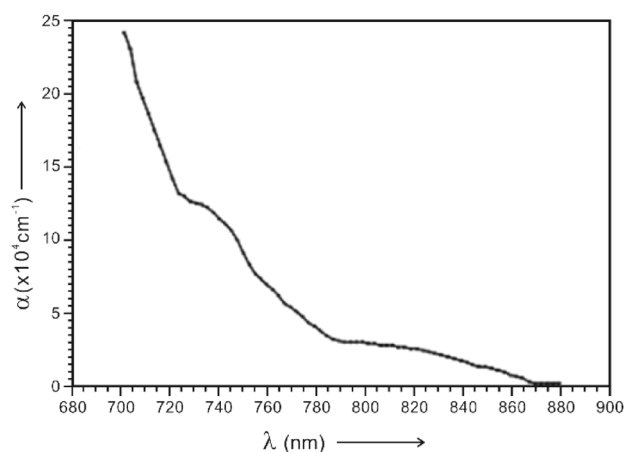
### 3. Absorption spectra analysis

The absorption spectra of the grown CdTe crystals were studied using the Beckman Model DK-A spectrometer over a wavelength range of 700–880 nm. The variation of absorption coefficient ( $\alpha$ ) with wavelength ( $\lambda$ ) is plotted in figure 2.

In order to attain better spectral resolution, the first derivative of the absorption coefficient with respect to the photon energy was evaluated. The transfer of oscillator strength resulting in a small perturbation of the first-order derivative component could be approximated by a second-order derivative in a Taylor-like expansion [45]. Thus,  $d\alpha/dE = d^2Q/dE^2$ ,  $Q$  representing the oscillator strength, and therefore it would be a second-order fluctuation in charge density.

The graph  $d\alpha/dE$  vs. energy ( $E$ ) in figure 3 reflected the fluctuations in the charge density within the grown sample showing two peaks, one around 1.75 eV and the second around 1.69 eV, with a fine structure. Thus, the two main peaks revealed a two-band transport due to splitting of the conduction band into two partially filled bands—one bonding and another anti-bonding. Such complex band-edge deformation related bonding and anti-bonding states were observed in CdTe by Hong *et al* [46]. Exclusive study on bonding and anti-bonding states in CdTe was reported by Liu *et al* [47], Park *et al* [48] and Shepidchenko *et al* [49]. Also, a blue shift was observed along with the splitting of bands as shown in figure 3. The observed shifting of absorption edge to higher energy was due to Burstein–Moss blue shift by the presence of excess Te in grown p-type CdTe. There were reports by Narayanan and Deepak [50] on Boron-Nitrogen co-doping in ZnO, and Hemathangam *et al* [51] on Zn-doped  $\text{Cu}_2\text{S}$  showing Burstein–Moss blue shift in p-type semiconductors.

Further peaks were observed at 1.63, 1.57 and 1.5 eV, as in figure 3. Albin *et al* [52] and Halliday *et al* [53] had



**Figure 2.** Absorption coefficient ( $\alpha$ ) vs. wavelength ( $\lambda$ ) of the grown CdTe.

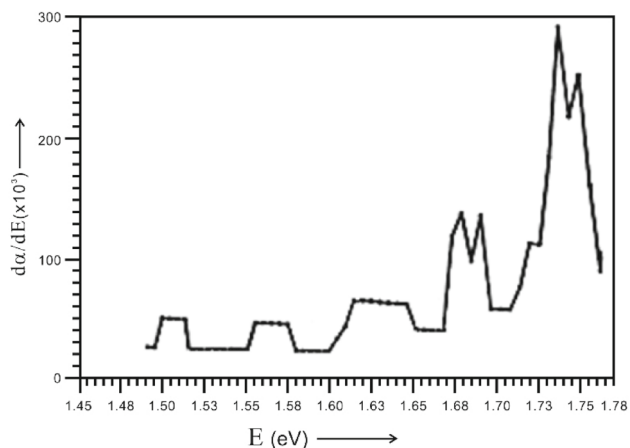


Figure 3. Variation of  $d\alpha/dE$  vs.  $E$  of CdTe.

reported similar acceptor-bound excitons in Te excess CdTe. Such a multiple step absorption process at various energy band regions is due to the presence of interstitial Te levels at Cd vacancy sites [54]. These peaks indicated the distributions of charge carriers among the localized states within the forbidden gaps owed by extrinsic impurities—in this case, the inhomogeneous distribution of excess Te. The high concentration Te would be highly confined and localized in CdTe lattice leading to peak broadening because of the overlapping of neighbouring Te impurity sites, which would result in the broadening of impurity levels. Kotani *et al* [55] and Pal *et al* [56] reported the linewidth broadening of inter sub-bands due to dopant concentration. Consistency in similar distribution of  $d\alpha/dE$  vs. energy ( $E$ ) curve of figure 3 was exhibited by CdTe samples obtained from repetitive growth cycles.

The various powers of absorption coefficients were computed and plotted against photon energy for understanding the inherent nature of electronic transitions in the grown CdTe [57]. The square of absorption coefficient ( $\alpha^2$ ) plotted against the photon energy in figure 4a revealed two transitions: (a) a direct one in figure 4b, satisfying  $\alpha = A(h\nu + E_g)^{1/2}$  at 1.454 eV, which matched with the estimated bandgap of the high resistivity measurement of grown CdTe by four-probe method [10], and (b) an indirect transition bandgap in figure 5, satisfying  $\alpha = A(h\nu + E_g \pm E_p)^2$  at 1.502 eV and phonon energy of 0.048 eV.

Apart from these two transitions, the  $(\ln \alpha)^{2/3}$  vs. photon energy plot showed a straight line, at the in-between region as in figure 6. This was due to the tunnelling of charge carriers from valence band to conduction band as a result of the band bending caused by the internal electrical field leading to tail states. A band tailing at lower energies below 1.525 eV was observed. The ‘Urbach tail’ [58] appeared between 1.503 and 1.485 eV was of the order of 0.018 eV. This revealed a shift in the optical absorption edge with

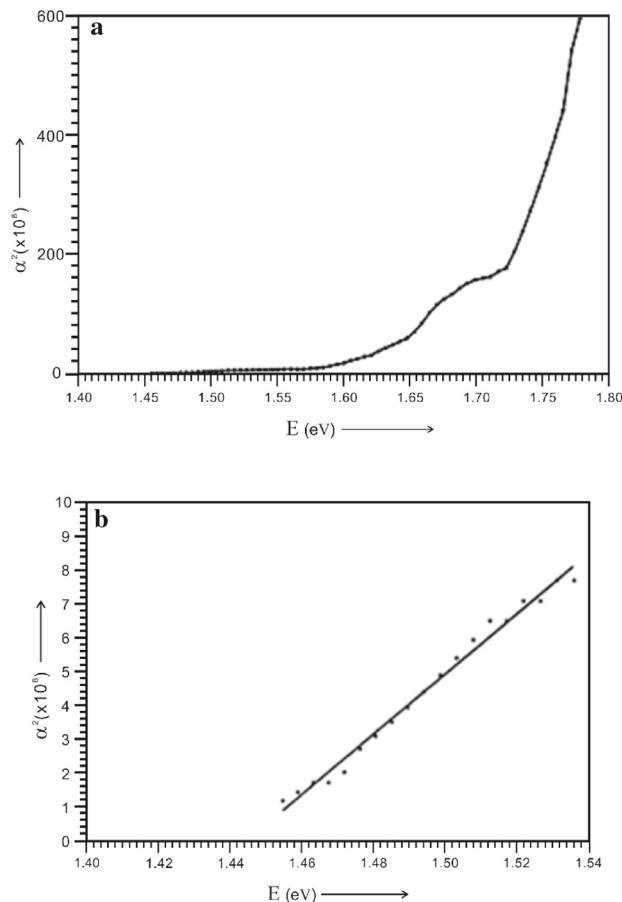


Figure 4. (a) Variation of  $\alpha^2$  vs.  $E$  of CdTe. (b) Variation of  $\alpha^2$  vs.  $E$  of CdTe representing direct transition.

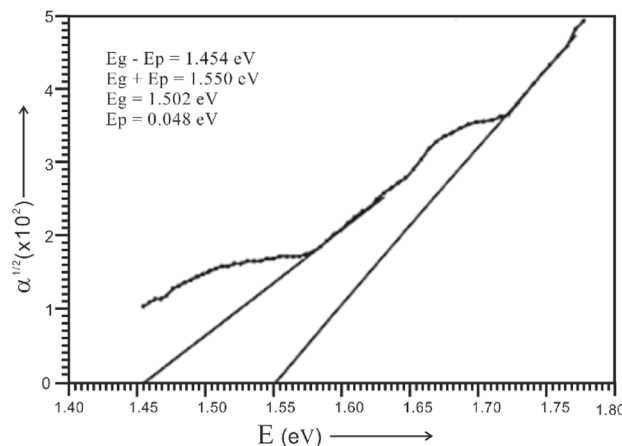
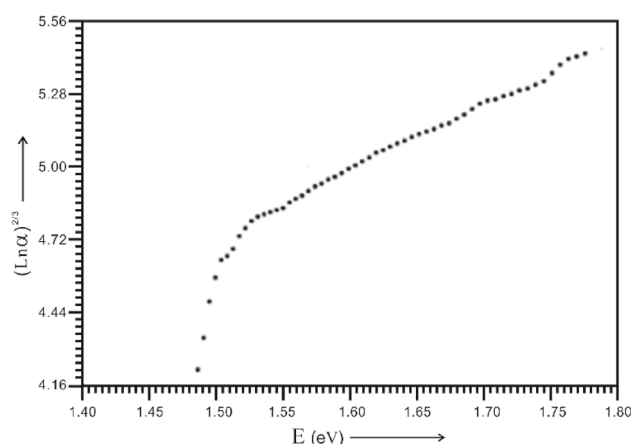


Figure 5. Variation of  $\alpha^{1/2}$  vs.  $E$  of CdTe representing indirect transition.

internal electric field responsible for the tunnelling of charge carriers [59] given by,

$$\alpha = Ae^{-\left(\frac{\gamma(\omega_G - \omega)^{3/2}}{E}\right)},$$

where  $\gamma = \frac{4\sqrt{2}\hbar\mu}{3e}$ ,  $\hbar\omega_G$  equal to 1.55 eV, which is the average indirect bandgap energy values where the straight



**Figure 6.** Variation of  $(\ln \alpha)^{2/3}$  vs.  $E$  of CdTe representing band tailing.

portion of the plot  $(\ln \alpha)^{2/3}$  vs.  $h\nu$  ends in figure 6,  $E$  the internal electric field,  $\mu$  the reduced band mass and  $\omega$  the external varying frequency.

The analysis presented in figure 6 confirmed the existence of a strong internal electric field in the grown CdTe rising from the degenerately doped crystalline semiconductor [60] due to excess Te present internally. Alteration in the profile of the fundamental absorption edge of a semiconductor induced by strong electric fields will lead to correlated changes in the refractive index [61]. The electric field-dependent changes in refractive index could lead to further optoelectronic applications [62].

#### 4. Conclusion

The analysis of the absorption spectra of p-type, tellurium excess and hexagonally structured cadmium telluride crystals grown from vapour phase having conductivity  $2.529 \times 10^4 (\Omega \text{ cm})^{-1}$  and carrier concentration  $1.425 \times 10^{16} \text{ cm}^{-3}$  exhibited the presence of both direct and indirect bandgaps, with an indirect transition bandgap at 1.502 eV and phonon energy 0.048 eV. The control of stoichiometry and thereby quantifying the presence of Te in such unconventional vapour phase growth of CdTe is a fascinating line that could supplement the correlation of conduction mechanism and optical properties of the material and could be taken up as the further extension of the current study. The tail states generated by the internal electric field leading to band bending and the tunnelling of charge carriers could lead to further applications in similar systems.

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