

## REVIEW

# Comprehensive Review on CdTe crystals: Growth, Properties, and Photovoltaic Application

Bibin John<sup>1</sup>, S. Varadharajaperumal<sup>2</sup><sup>1</sup>Department of Physics and Electronics, CHRIST - Deemed to be University, Bangalore, India<sup>2</sup>Center for Nanoscience and Engineering (CeNSE), Indian Institute of Science, Bangalore, India

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## ABSTRACT

Despite the deep interest of materials scientists in cadmium telluride (CdTe) crystal growth, there is no single source to which researchers can turn for comprehensive knowledge of CdTe compound semiconductor synthesis protocols, physical characteristics, and material performance. Considering this, the present review work focuses on bridging these shortcomings. The CdTe crystals with direct band gap ( $E_g$ ) have been in limelight in the photovoltaic application (PV) as the optoelectronic properties such as  $E_g$  (1.49 eV), absorption coefficient ( $\sim 10^5 \text{ cm}^{-1}$ ),  $p$ -type conductivity, carrier concentration ( $6 \times 10^{16} \text{ cm}^{-3}$ ), and appreciably high mobility ( $1040 \text{ cm}^2/\text{V s}$ ) at the room temperature are reported, which are optimum for solar cells. Additionally, Cd-based crystals have also been widely studied and implemented in the field of  $\alpha$  and  $\gamma$ -ray radiation detectors because of their extraordinary advantages like a large atomic number, low weight, high mechanical as well as thermal stability, flexibility, and the availability of the constituent materials. Cadmium telluride has demerits like toxicity (ecological damage) and high chances for defects/dislocations due to high thermal conductivity at melting temperature and high melting temperature, which will complicate the growth of stoichiometric CdTe crystals at high temperatures. Even though CdTe has the aforementioned issues, on the other hand, the absorber material reached a milestone (solar cell efficiency in the order of 22%), which enhances the attractiveness of this binary compound more and more in the field of crystal growth technology. In this regard, the review work focused on the periodic evolution of the growth protocols until now for the production of bulk, good quality CdTe crystals. The different synthesis methods, characterization, and recent progress in the field of crystalline CdTe were discussed briefly. Important physicochemical characteristics are presented in the tables and remaining issues due to chemical in-homogeneity, defects, imperfections, etc., have been discussed, which could facilitate the researchers who are working on this class of compound semiconductors. The applications of CdTe crystals to PV fields are also discussed separately in this review paper.

**Index Terms**—Cadmium telluride (CdTe), traveling heater method, horizontal traveling heater method, sublimation method, dislocation density, photovoltaic application

## I. INTRODUCTION

Compound semiconducting materials have gained tremendous attention in the past few years as basic absorber materials for photovoltaic applications. Fundamental characterization and studies of cadmium telluride (CdTe) crystals began around 60 years ago due to their potential application in optical and electrical fields [1]. This material comes under the category of II–VI binary compound semiconductors. Cadmium telluride is one of the technologically important semiconductor materials with a range of applications that require high-quality and defect-free substrates. It is also used as a radiation detector because of its large average atomic number ( $Z = 50$ ), relatively large stopping power, and high resistivity at room temperature [2]. It is an economical, earth-abundant material, which facilitates its value in sustainable development in electronic as

well as photonic systems [3, 4]. Like other solar cell absorbers such as Si and GaAs, CdTe also has an optimum bandgap (1.49 eV) and high absorption coefficients near the band edge, making it an excellent material for photovoltaic technology [5]. Even though CdTe possesses ecological damage due to toxicity, this semiconductor is a robust and chemically stable material for this reason. It can be deposited with a large variety of methods, making it very much ideal for production in a large area. Along with this, CdTe has a wide range of applications; however, the synthesis of this compound with high quality and stoichiometry is still difficult. The complexity of growing chemically homogeneous large dimensional crystals has hindered the fast development of many devices based on the CdTe substrate. Therefore, the synthesis technologies for the growth of high-quality CdTe and related compounds have rapidly been enhanced in recent

**Corresponding author:** Bibin John, bibin.john@res.christuniversity.in

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decades [6]. Various crystal growth methods have been developed for the production of CdTe materials, like sublimation, the vertical Bridgman method, horizontal traveling heater method, traveling solvent method, and Liquinert-processed vertical Bridgman (LPVB) or detached growth method, etc. [7-12]. Rudolph et al. [13] reported that there is a strong influence between the stoichiometry and electrical as well as optical properties of the crystals. Hence, the control of composition during the crystal growth process is extremely important both from the physical and structural points of view. However, this homogeneity problem is one of the major drawbacks of the CdTe crystals grown from the melt due to the lack of thermodynamic data, growth methods, and physicochemical properties. Generally, the growth of CdTe single crystals with the Czochralski method has not been very successful. The CdTe crystals are always characterized by a coarse-grained structure with  $\sim 1 \text{ cm}^3$  of crystallites and a high number of twin lamellae. The inhomogeneity and steep axial temperature gradient of the melt are the primary sources of high defect content. Al-Hamdi et al. [14] have discussed the safe, efficient, and cost-effective growth of crystalline CdTe samples from the elements Cd and Te, which is rather challenging in a silica-sealed growth ampoule owing to the large vapor pressure (above 1 atm) of the cadmium element. The preparation of the high melting point CdTe compound from the low melting point elements tends to exhibit unreacted molten Cd and Te as the mixture is heated. This is due to the high vapor pressure of elemental cadmium; the pressure from the overheated pools of Cd can increase well above 1 atm at high temperatures. On the other hand, this may pose explosion risks in traditional synthesis methods using sealed quartz ampoules [15]. Also, the probability of over depositing un-reacted Cd is higher in larger-volume loads; therefore, the scalability is limited by the strength of the quartz ampoules. Generally, the CdTe growth methods and the quality of the material naturally affect the cost of CdTe device technologies. Small-volume synthesis of CdTe in sealed silica ampoules tends to be expensive due to high labor and consumable costs. Therefore, it is imperative to explore the appropriate and systematic review of the CdTe synthesis processes to finalize the robust, scalable, low-cost CdTe feedstock growth that provides high purity, doping control, and the flexibility to produce from both Cd and Te rich melts when necessary. Thus, this review paper mainly deals with the history of CdTe research, crystallization of good-quality crystals, material properties, structure and bonding, the electronic structure of CdTe, optoelectronic properties, defects, applications, and conclusion.

## II. HISTORY OF CdTe RESEARCH

Cadmium telluride is an II–VI family chalcogenide compound that has a zinc-blend crystal structure that belongs to the cubic

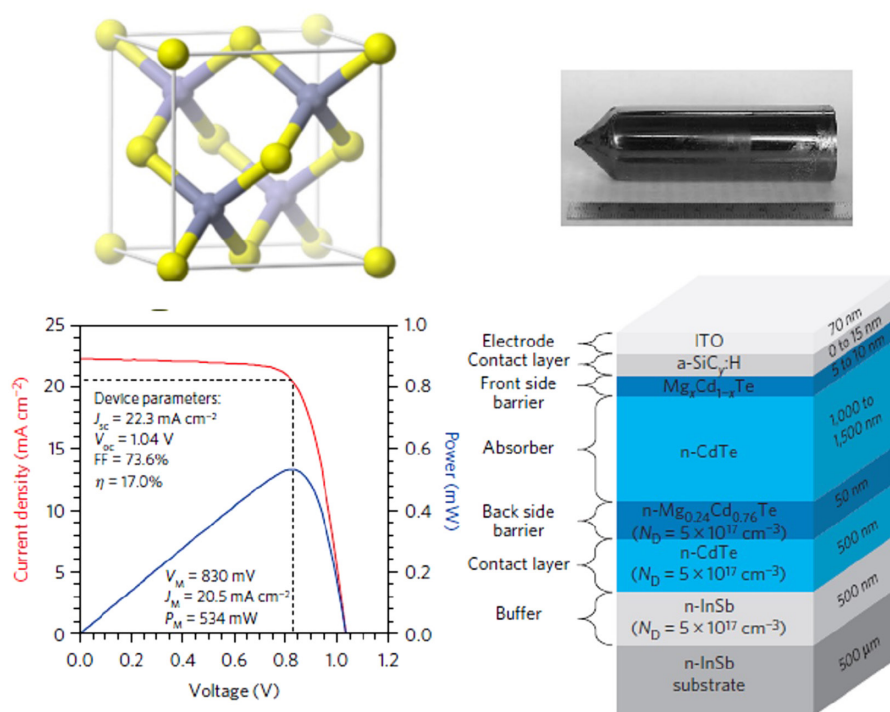
noncentrosymmetric space group  $F\bar{4}3m$  ( $T_d^2$ ). This crystal is iso-structural with diamond except for the alternation of the two different elements (Cd and Te) on the successive lattice sites. The CdTe compound has a long research history; all these findings are beneficial to unearthing the physical properties of the crystal through a systematic review of these published works. Hence, the present review article attempts to spotlight or present the various growth methods for the production of high-quality CdTe crystals and their physical as well as chemical characteristics for photovoltaic applications. The schematic depiction of the atomic model of the zinc-blende structure is depicted in Fig. 1a. Furthermore, the precisely calculated lattice parameters of the CdTe samples,  $a = 6.47832 \text{ \AA}$ , are almost identical to standard data [13, 14]. In the past few years, researchers have developed new crystal growth technologies for the production of  $\sim 1 \text{ kg}$  size of CdTe crystals from the elemental precursors of Cd and Te with high purity for photovoltaic applications [14]. From the 1960s to the 2000s, the number of research reports on the physical properties of CdTe gradually increased. As a result, the basic understanding of the structural, optical, and electrical properties of the material expanded significantly [1-5, 7, 9-10, 12-15]. It is interesting to note that the role of the CdTe semiconductor is transformed from being a radiation detector to being an absorber medium in photovoltaic applications [16]. Fig. 1b shows the image of a grown CdTe:Ge single crystal with a 25 mm diameter that can be cleaved into wafers for diverse device applications. The current density versus voltage plot of the device (Fig. 1d) is depicted in Fig. 1c. This shows that the CdTe-based heterojunction solar cell has a high fill factor of 73.6% and power conversion efficiency of 17%, which is close to the famous silicon-based photovoltaic devices. The inset of Fig. 1c shows the other solar cell parameters obtained from the device. In the current era of solar cell fabrication, most thin films have different absorber or window layers of various materials to absorb or collect the maximum number of photons from the sunlight (Fig. 1d).

## III. MATERIAL PROPERTIES

In general, the major factor affecting the conversion efficiency of the solar cell is the quality of the CdTe absorber material. The yield of defect-less CdTe crystals is limited due to the formation of Te clusters in the melt during the melt growth process. This is a special property of the II–VI group materials [17]. Hence, pure phase, good crystalline, and large grain size are inevitable criteria for the semiconducting materials for photovoltaic applications. The low melting point and vapor pressure help the synthesis of this crystal in the atmospheric pressure furnace with the utilization of quartz ampoule [6]. The high absorption coefficient of this sample enhances the effective absorption of a large amount of light energy and thereby generates more photogenerated carriers before their recombination. Also, the direct absorption of solar radiations without any momentum assistance makes the CdTe absorber more attractive than crystalline silicon. In addition to these optical parameters, melt-grown crystalline CdTe exhibits less resistivity and high carrier mobility at room temperature, which is suitable for PV applications. A high internal electric field at the  $p$ - $n$  region ensures the separation of the electron–hole pairs. Hence, the selection of a suitable active absorber material for the absorption of light relies not only on the bandgap value but also on the other properties of materials, such as readily attainable  $p$ -type or  $n$ -type conductivity, charge–carrier lifetime,

### Main Points

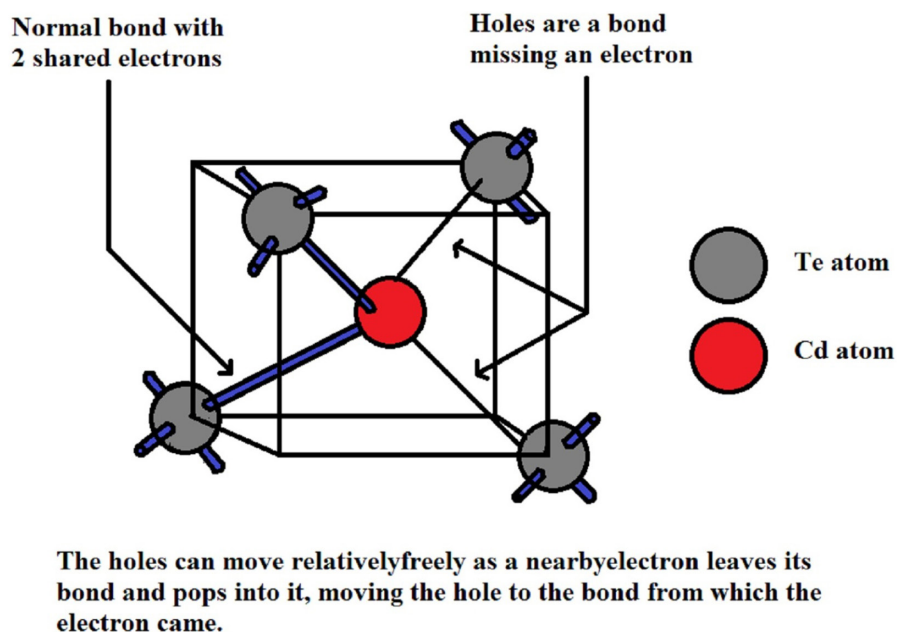
- Review of different growth methods for the production of good quality bulk cadmium telluride (CdTe) crystals.
- Comprehensive review of CdTe compound semiconductor synthesis protocols, properties, and performance.
- Suitability of bulk CdTe crystals for photovoltaic applications.
- Impact of growth method on the quality of CdTe crystals.



**Fig. 1.** (a) CdTe atomic structure, blue-shaded balls correspond to Te and yellow balls to Cd. (b) Image of CdTe:Ge crystal with 25 mm [16]. (c) Measured  $J$ - $V$  curve and associated device parameters. (d) Layer structure of the CdTe/ $\text{Mg}_x\text{Cd}_{1-x}\text{Te}$  DH solar cell with an  $\text{a-SiH}_y\text{-H}$  ( $y = 0$ –6%) hole-contact layer [3].

carrier concentration, dielectric constant, and low excitation binding energy. However, there is no single comprehensive research finding focusing only on the CdTe crystals for photovoltaic applications, despite the fact that CdTe is the second most popular solar cell active

layer. Therefore, in the present review work, the physicochemical properties of the CdTe crystals are tabulated in Table I. For the following reasons, the solidification of this binary compound with high quality is quite difficult:



**Fig. 2.** Two valance electron impurity (Cd) in a Te crystal is normally bonded except two of the bonds are missing the electrons, that is, is a hole.

- i) Thermal conductivity is very low because of which the dissipation of heat during the growth of the melt is difficult. Hence, a smooth solid–liquid interface cannot be easily achieved in the melt.
- ii) Shear stress is low, so dislocations are easily generated by thermal stress.
- iii) Stacking fault energy is low because of this, twins are easily formed.

#### IV. STRUCTURE AND BONDING

##### A. Basic Structure

Compound semiconducting materials are the central focus of crystal growth technology in the current era due to the huge revolutionary development witnessed in the field of optoelectronic devices. In particular, in the energy sector, like photovoltaic, fuel cells, hydrogen production, sensors, and detector applications. For harnessing energy from sunlight, the quality and purity of the absorber materials are essential, which can be achieved through the right absorber medium and their growth without any defects. From this point of view, CdTe has a relatively high atomic number compared to the other elemental photovoltaic material like silicon (Cd: 48, Te: 52, and Si: 14). The valance electronic configuration of cadmium (Cd) and tellurium (Te) atoms are  $4d^{10}5s^2$  and  $4d^{10}5s^2 5p^4$ , respectively. As the electronegativity of Te atoms is much stronger than Cd atoms, Te captures two electrons from the Cd atom which leads to a change in the electronic configuration of Cd from  $4d^{10}5s^2$  to  $4d^{10}5s^0$  and that of Te to  $4d^{10}5s^2 5p^6$ . Cadmium and Te were labeled in a black square box in the periodic table (see appendix, Fig. S1.). The physical and chemical parameters of the melt-grown CdTe crystals are also presented in Table I. These functional properties help the research of those who are working on the growth of low dislocation density semiconducting CdTe material. A large-dimensional stoichiometric CdTe compound has been mainly prepared using the melt growth method (Bridgman–Stockbarger). There are a few reports on the Czochralski technique (CZ), the traveling heater method (THM), the vertical gradient freeze technique, and the LPVB method [2, 5, 8, 11–13, 18–25] (Fig. 2). A brief account of crystal growth using the aforementioned techniques is explained in section 6. Cadmium telluride is a group II–VI semiconducting compound material having a zinc-blend crystal system and belongs to the cubic noncentrosymmetric space group  $F\bar{4}3m$  ( $T_d^2$ ). The schematic of the atomic replica of CdTe crystals is depicted in Fig. 3. The reported lattice parameter of the CdTe crystal is " $a = 6.47832 \text{ \AA}$ ," which is almost identical to recently reported data [16, 17]. The CdTe semiconducting materials grown by the LPVB method have a zinc-blend crystal structure as discussed by Sekine et al. [12].

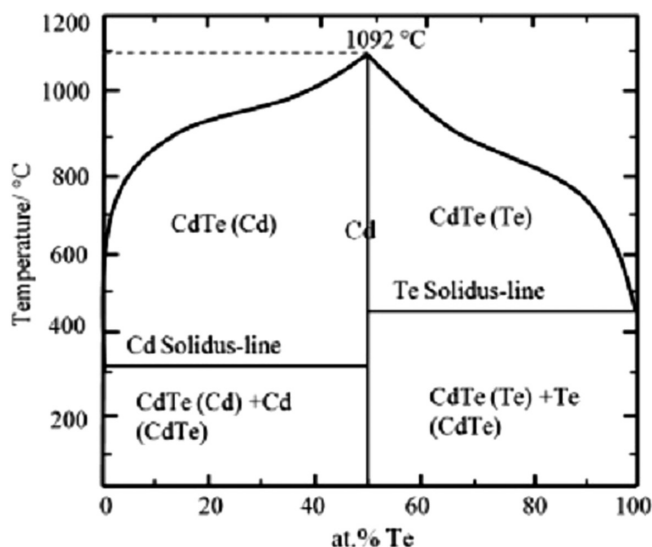
##### V. PHASE DIAGRAM OF CDTE

The engineering of crystals, as well as the fabrication of optoelectronic device, is very much essential to understand the response of CdTe crystal at different chemical composition. Fig. 3 shows the phase diagram of CdTe crystals. As compared to the phase diagram of other ternary or quaternary materials, the diagram of this sample is very simple. The melting point of the pure CdTe samples (50:50 at.%) was reported to be  $1092^\circ\text{C}$  as per the phase diagram, which is applicable for the monophasic as well as stoichiometric CdTe samples [26]. Suppose the atomic ratio of CdTe deviates from the 50/50 at.%

**TABLE I.**  
PHYSICO-CHEMICAL PROPERTIES OF CDTE CRYSTALS

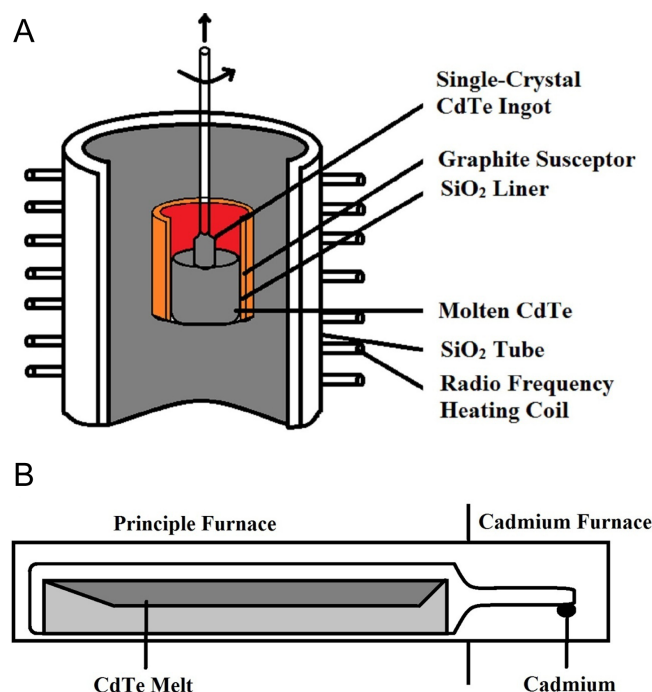
Properties of Material	Symbol	Value
Chemical formula		CdTe
Molecular weight	W	240.01
Group		Cadmium: 12 Tellurium: 16
Crystal structure		Cubic [11]
Lattice constant	A	$6.482 \text{ \AA}$ [11]
Dielectric constant		10.2
Hole mobility	$\mu_h$	$65 \text{ cm}^2/\text{V s}$
Electron mobility	$\mu_e$	$700 \text{ cm}^2/\text{V s}$
Carrier concentration	P	$6 \times 10^{16} \text{ cm}^{-3}$ [1]
Carrier mobility	$\mu$	$1040 \text{ cm}^2/\text{V s}$ [1]
Density	D	$5.85 \text{ g/cm}^3$
Melting point	M.P	$1092^\circ\text{C}$ [17]
Boiling point	B.P	$1130^\circ\text{C}$
Young's modulus	Y	$3.7 \times 10^{11} \text{ dyne/cm}^2$
Rupture modulus		$2.2 \times 10^8 \text{ dyne/cm}^2$
Refractive index		2.67
Band gap	$E_g$	$1.5 \text{ eV}$ (room temperature) [18]
Nature of band gap		Direct optical band gap [18]
Absorption coefficient	A	$>10^5 \text{ cm}^{-1}$ [18]
Thermal expansion coefficient		$5.9 \times 10^{-6}/\text{K}$
Specific heat capacity	H	$0.21 \text{ J/g K}$
Thermal conductivity	$\Sigma$	$\sim 4 \text{ W/m K}$ [11]
Thermal expansion coefficient		$5.9 \times 10^{-6}/\text{K}$

during the crystal growth process, the material will phase separate into CdTe and Cd or Te, whichever has the greater composition. Because both Cd and Te have higher vapor pressure than crystalline CdTe, these elemental components will try to re-evaporate before they could be incorporated into the growing crystal [27]. Minute changes in the purity of the crystal result in large sub-liquidus regions of liquid + CdTe with a Cd-rich liquid phase for Cd-enriched compositions and a Te-rich liquid for Te-rich compositions. Fig. 4 shows that Cd-rich compositions melt at  $322^\circ\text{C}$ , solidus temperatures and  $450^\circ\text{C}$  for Te-rich compositions. This represents the melting points of pure Cd and pure Te, respectively. Hence, this graph represents that for even small deviations from stoichiometric CdTe, some amount of



**Fig. 3.** Phase diagram of CdTe crystal for the effect of stoichiometry and temperature [27].

liquid phase will be present above 322°C for Cd-rich compositions and above 450°C for Te-rich compositions. The relative amounts of liquid will increase as a function of the amount of deviation from pure stoichiometry. This has implications for the processing of CdTe devices that are not chemically pure and which may be processed at temperatures above 322°C or 450°C, depending on the process methodology. Determination of elemental percentage also suggests that for equilibrium conditions, temperatures greater than 600°C



**Fig. 4.** Schematic of the (a) Czochralski growth apparatus and (b) liquid encapsulated Czochralski growth apparatus.

can exhibit a large amount of Te or Cd compared to temperatures below 500°C [26]. The stoichiometric deviation adversely affects all the physical properties, including the performance of solar cell device. Therefore, the phase diagram will help the crystal growers to adopt a suitable growth method for the production of high-quality CdTe crystals. The phase diagram of the CdTe samples also facilitates the fabrication of devices without many defects or problems.

## VI. BULK CRYSTALLIZATION OF CDTE CRYSTAL GROWTH

### A. Melt Growth Method

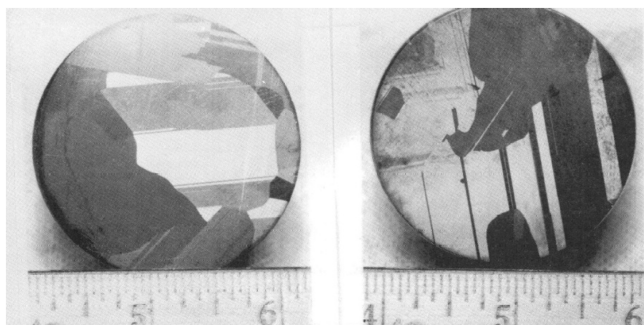
#### 1) Czochralski Process and Liquid Encapsulated Czochralski (LEC) Method

The growth of crystals by pulling from the melt was first introduced by Czochralski in the year of 1971. It results in a single crystal with fewer imperfections and is free of the physical constraints imposed by the crucible. Fig. 4a shows the schematic depiction of the Czochralski growth apparatus. The necessity to maintain the melt in a crucible often acts as a contamination source, which is the main disadvantage of this growth approach. Initially, a tiny single crystalline CdTe seed is placed on top of the molten material of the purified CdTe. After a small interval of the period, the seed crystal is slowly elevated up to less than 10 cm/h and rotated to attain proper homogeneity. As the CdTe semiconducting compound rises slightly from the melt, CdTe freezes on its surface, extending the single-crystal structure. The final product is most probably a cylindrical ingot, or boule, typically the container's diameter and many times that in length. Meantime, liquid encapsulated Czochralski (LEC) method has been developed for the growth of CdTe crystals in the 1970s but it was unsuccessful. The Czochralski and LEC methods are found to be unsuitable for the synthesis of CdTe compounds due to their tendency to form twins during the growth process. Hobgood et al. [28] have grown CdTe ingots of 50 mm in diameter and weighing up to 1 kg by precisely adjusting the synthesis parameters (in a modified Melbourn crystal puller). However, only a few LEC growth trials were conducted for the growth of CdTe compound semiconductors because this synthesis method is not appropriate for the growth of CdTe crystals. These authors investigated the microstructure of the CdMnTe ingots and observed a mosaic-like array of sub-grains corresponding to misorientations from the true (111) growth axis. Also, the etch pit density (EPD) is reported as being in the order of  $\sim 10^6 \text{ cm}^{-2}$ . The schematic diagram of the LEC growth apparatus is depicted in Fig. 4b. The value of the EPD of the CdTe is larger than the other compounds and elemental semiconducting crystals. The addition of magnetic fields (greater than 2000 G) helps to adjust the thermal fluctuations in the LEC growth of CdTe and CdMnTe melts, which control the twinning of the crystals. The axial temperature gradient of the LEC method is high, leading to the development of dislocation densities in the final product, which may adversely affect the material properties [7].

#### 2) Heat Exchanger Method (HEM)

Because of this demerit, the poor thermal conductivity of the CdTe crystal prevents the growth of the latter via the directional solidification growth method. It is very difficult to control the solid-liquid ( $\beta$ - $\alpha$ ) interface shape during crystal growth. Also, it is well known that the planar solid-liquid interface is favorable for the growth of high-quality samples. Since it has difficulty in controlling the shape and the  $\beta$ - $\alpha$  interface and the movement during the synthesis process,



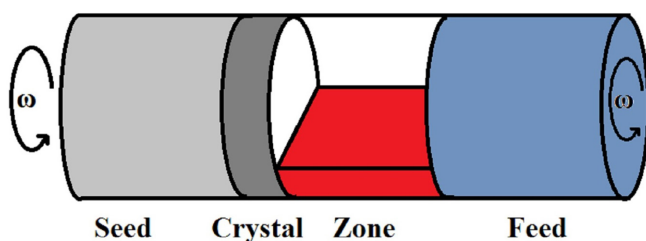


**Fig. 5.** Structure of (a) top and (b) bottom surfaces of 5.5 cm diameter CdTe ingot grown in HEM. HEM,

spontaneous nucleation will occur during the growth process in unseeded crystal growth. On the other hand, 5–7.5 cm diameter CdTe ingots were grown using the heat exchanger method (HEM). Khattak and Schmid [29] have reported that CdTe crystals with high stoichiometry and large twin-free samples could be obtained through the heat exchanger growth method. The EPD is calculated in the range of  $10^3$ – $10^5$   $\text{cm}^{-2}$ . The dislocation density of the CdTe crystals grown using this method is lower compared to the Czochralski technique. Most of the HEM-grown CdTe samples have *p*-type conductivity, but the resistivity is found to be high (in the order of  $10^5$   $\Omega$  cm). The optical properties like absorption coefficient have been reported in the range of  $0.07$   $\text{cm}^{-1}$ . In order to nucleate larger grains, higher superheat temperature treatment of  $80^\circ\text{C}$  in 44 hours was utilized. Fig. 5 shows the cleaved CdTe structures, the top and bottom surfaces of the 2 cm long and 5.5 cm diameter wafer with 400 g ingot.

### 3) Horizontal traveling heater method (HTHM)

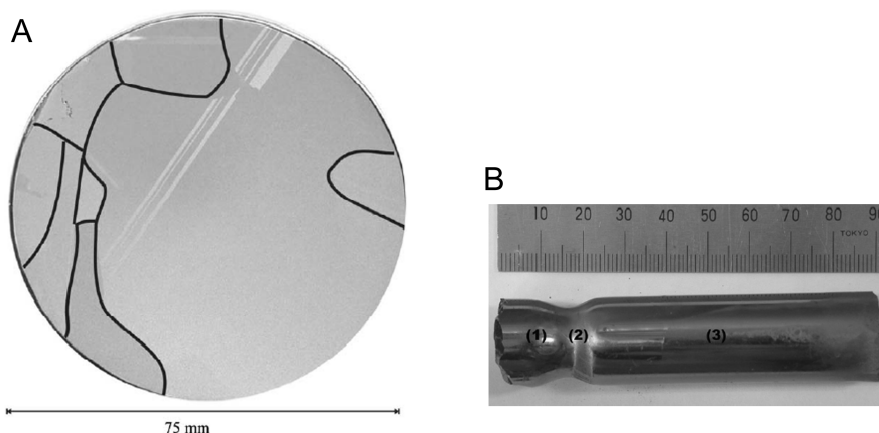
The horizontal traveling heater method (HTHM) was implemented by Genzel et al. [30] for the growth of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  crystal. Rotation of the ampoule is necessary for the crystallization of the whole material in a cylindrical cross-section of the ingot with respect to the partially filled solution zone (Fig. 6). It is important to note that the HTHM crystal growth technique required complex experimental equipment to grow high-quality crystals, without presenting a definite advantage over vertical THM with ampoule rotation which is much easier to implement.



**Fig. 6.** Schematic representation of a horizontal traveling heater method crystal growth arrangement [9].

### 4) Bridgman-growth method

To the best of my knowledge, Shin et al. [31] are the first researchers who grew CdTe compound semiconducting material through the Bridgman method in the year 1983. However, they observed the presence of Te precipitate on the crystal surface and also predicted that there is a correlation between the presence of Te agglomerates and optical transmission. Route et al. [19] have investigated the melt/solid interface during vertical Bridgman growth with the aid of the autoradiography technique. Melt interfaces were controlled as convex shapes through thermal modifications, but no significant improvement was seen in the grain structure. Oda et al. [32] have grown CdTe single crystals by vertical Bridgman method with a translation rate regulated from 1 to 5 mm/h. The CdTe crystals were chemically etched using 3% of  $\text{Br}_2$  methanol etchant for 3 minutes to calculate the dislocation density. Bridgman growth method is one of the economic and simple melt synthesis approaches for bulk crystallization, in which the ingot material is filled in a closed quartz/glass ampoule and melted under varying temperature gradients with an optimized translation rate. Many researchers have adopted the Bridgman growth method, because of its simplicity and relatively large growth rates as compared with the solution and vapor growth [20, 33–42]. Fiederle et al. [20] have synthesized CdTe crystals with 25, 45, and 75 mm diameters by the vertical Bridgman method, respectively. The reduced twins and growth of large single-crystalline grains in the order of  $40 \times 40$   $\text{mm}^2$  helped to improve the crystallinity of the latter. The CdTe:Ge crystal of 75 mm diameter wafer with only seven small grains, two twins, and a large single crystal is grown by the modified Bridgman technique. To produce a good-quality wafer (Fig. 7a), high pure-source materials of 7N purity were selected, that is, high-quality quartz ampoules coated with carbon, also the temperature profile of the furnace was modified [20]. Modified Bridgman technique with the fabricate furnace, which allows the minute regulation of different degrees of superheating of the ingot melt before the growth process, is employed to synthesize CdTe single crystals by Saucedo et al. [38]. High-quality CdTe crystals with appreciable structural perfection and reduced Te precipitate concentration through modified Bridgman method with artificial seeding. Fig. 7b shows the CdTe crystal image grown via the modified Bridgman method; from the latter Fig. 7a, it is clear that the synthesized semiconductor has a 9 cm length with a 1 cm diameter. Also, region (2) represents the interface between seed and crystal, (1) corresponds to the seed material, and (3) is the grown crystal portion. The interface will determine the quality of the crystal; it may be planar, convex, or even concave. The critical optimization of the liquid–solid interface will play a vital role in all types of melt growth methods. There is a piece of wonderful information about the interface shape discussed by Cheuvart et al. [43]. On the other hand, the transverse gradient induces a strong thermal oscillation and turbulence, and the convection in a liquid increases the effective liquid thermal conductivity  $K_{\text{liq}}$  as well as the ratio  $K_{\text{liq}}/K_{\text{sol}}$ , which directly influences the shape of the liquid–solid interface during the crystal growth. Casagrande et al. [44] have grown 64 mm diameter single crystals of CdTe through a multi-zone vertical Bridgman furnace. Melt adhesion or spurious nucleation was optimized with the careful preparation and selection of the ampoule. The interface curvature



**Fig. 7.** (a) CdTe:Ge wafer with 75 mm diameter [18], (b) Typical CdTe crystal obtained by the modified Bridgman technique. The marked zones correspond to the seed to (1) the interface between the seed and the crystal, (2) the as-grown crystal (3) [36].

as well as the thermal stress during the crystallization portion of the boule is minimized by adjusting the hot and cold zone temperatures. They suggest that the post-solidification process is primarily important to reduce the slip defects in crystals. Bruder and co-workers [45] reported that when the cooling rates are greater than  $10^{\circ}\text{C}/\text{h}$  will result from an increase in the strain and low-angle grain boundaries. The high-pressure Bridgman technique offers an appreciable growth rate and good control of purity and chemical homogeneity, and the grown CdTe crystals gain size is comparable with the ingot formed inside the quartz ampoule synthesized by the vertical Bridgman method [46]. The careful optimization of melt–solid interface (to attain atomically flat interface) by controlling growth conditions like rotation speed, translation velocity, supercooling, etc., was reported by several authors [47–50].

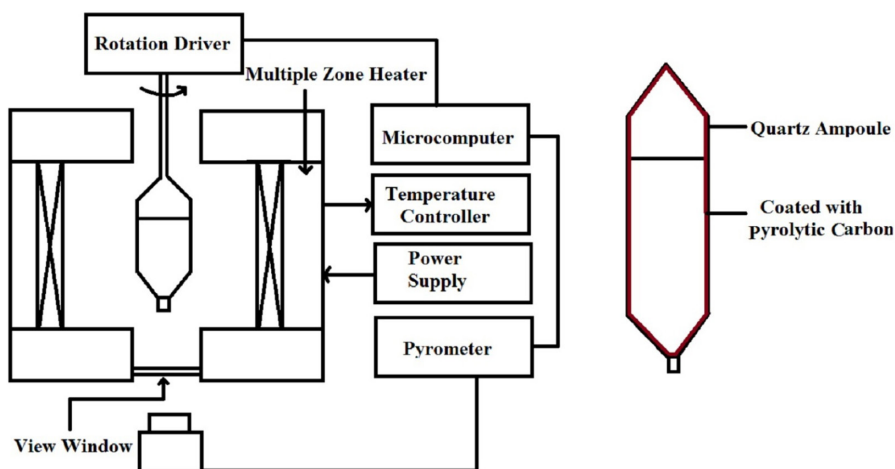
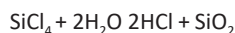
##### 5) Gradient Freeze Method

Tanaka et al. [51] reported that the vertical Bridgman and gradient freeze growth methods are appropriate for the crystallization

of high-quality large CdTe crystals. In the gradient freeze method (Fig. 8a), the charge CdTe materials were sealed in an evacuated quartz ampoule (Fig. 8b) under a pressure of  $10^{-6}$  torr. The pyrolytic carbon is coated inside the wall of the ampoule to avoid the reaction of residual Cd-oxide with the quartz. The pyrolytic layer will help to eliminate the contamination from oxides and the impurity particles from the inner walls of the ampoule as well as to prevent the adhesion of the ingot to the crucible inner wall [29]. The gradient freeze-grown CdTe crystals were found to be stoichiometric in the ratio of Cd:Te as 49.9:50.1.

##### 6) Liquinert-processed vertical Bridgman (LPVB) or Detached growth method

The single crystals of CdTe were grown by the LPVB method. In this method,  $\text{SiCl}_4$  strongly reacts with  $\text{H}_2\text{O}$ , following the reaction formula:



**Fig. 8.** (a) Schematic block diagram of a gradient freeze growth system [45] and (b) quartz ampoule for crystal growth.

As per the chemical reaction, the water content in the ampoule is adequately removed to obtain the liquinert state. Liquinert means that liquid is in an inert state. Thus, here  $\text{SiCl}_4$  was used for the reduction of residual  $\text{H}_2\text{O}$  in the growth container, raw material, and atmosphere during synthesis. The liquinert process for CdTe crystals is a two-step procedure, where the first stage involves the removal of the oxides from the base elements Cd and Te for the preparation of high-quality CdTe crystals, various processes such as vacuum distillation, reduction with hydrogen, and chemical etching, etc. Sekine et al. [12] have grown CdTe single crystals by adopting the LPVB method. The following are the emergent problems in CdTe crystal growth:

- (i) Wetting and sticking on the crucible during crystal growth.
- (ii) Avoiding crucibles with high thermal conductivity such as carbon.
- (iii) Obtaining crystal growth with a stoichiometric composition.

The LPVB growth method is schematically illustrated in Fig. 9a. This schematic depiction of the experimental route systematically explains the various steps involved in this growth method. Photograph and XRD profile of the LPVB grown single crystal and the cleaved portion are shown in Fig. 9b-c. The single crystalline nature and the growth direction of the CdTe along (110) plane were confirmed with the assistance of X-ray diffraction (XRD) by Sekine et al. [12]. Yamada et al. [52] synthesized CdTe crystals in the bare quartz

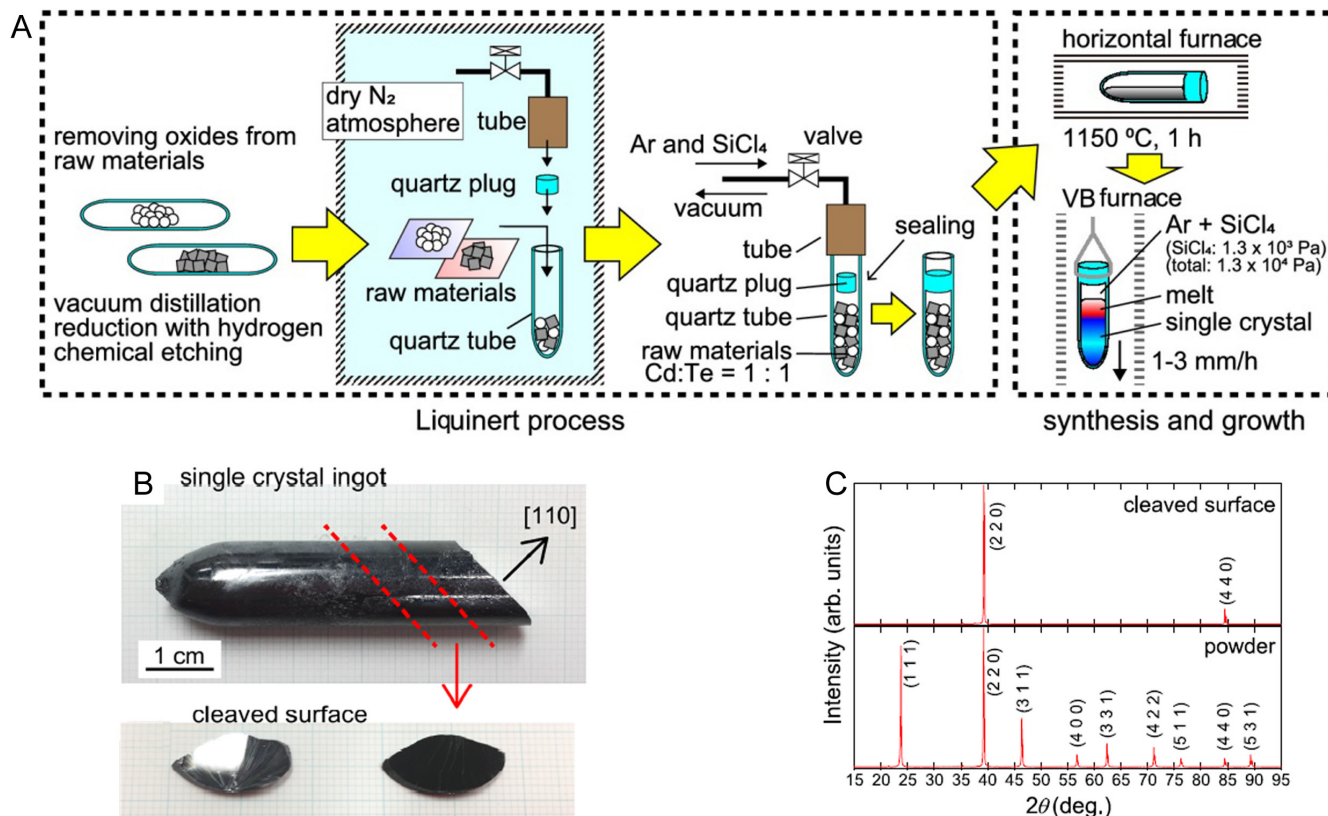
ampoule utilizing the vacuum distillation method, which helps to eliminate the presence of oxygen from the raw materials Cd and Te.

## B. Vapor Growth Method

### 1) Sublimation Method

As reported by Teramoto [53], the bulk form of cadmium telluride binary chalcogenide semiconductor is grown from the vapor phase by the sublimation method, and recrystallization of the material is performed along a temperature gradient in the  $\text{N}_2$  atmosphere. The vapor-deposited CdTe crystals have a cubic zinc-blende structure. The growth chamber used for the synthesis of single-crystalline CdTe through the sublimation method is portrayed in Fig. 10. High crystalline CdTe material is prepared mostly through melting by the Bridgman and zone-melting methods. The vapor growth method is not fair enough for the production of bulk crystals, but vapor-deposited crystals are superior for studying the growth mechanism and stoichiometric preparation of compound materials and probing various physical properties on as-grown faces. Important factors that affect the quality of the sublimation of CdTe crystal are listed below:

1. sublimation speed of CdTe precursor powder (function of the temperature of the powder),
2. particle size,
3. follow rate of the nitrogen carrier gas.



**Fig. 9.** (a) Schematic depiction of the LPVB furnace and crystal growth; (b) Photograph of CdTe single crystal and the cleaved portion and (c) XRD profile of the cleaved crystal as well as the powdered material [12]. LPVB, Liquinert-processed vertical Bridgman.



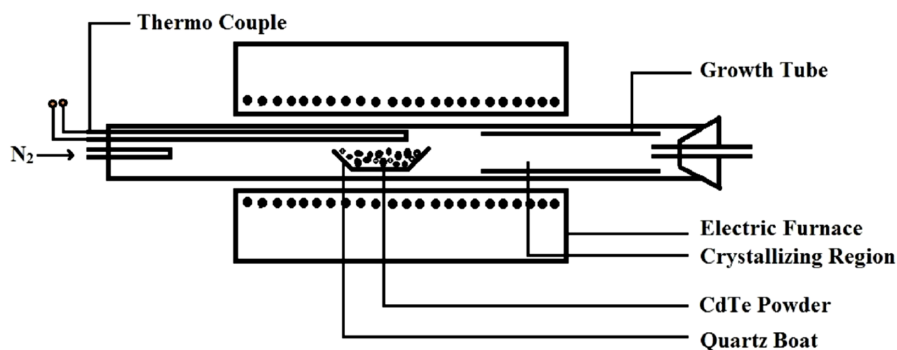


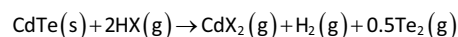
Fig. 10. Apparatus for crystal growth [45].

The vaporized CdTe powders are carried by the flow of nitrogen gas toward the boat region/low-temperature region of the growth zone. The problem associated with this vapor transport method is the contamination due to carrier agents during the synthesis process. This will adversely affect the physical properties of the CdTe crystal. The crystal habits depend on different factors such as (1) sublimation temperature, (2) growth temperature, and (3) flow rate of the nitrogen gas. The author [53] also reported that it is not possible to determine an accurate degree of supersaturation ( $S$ ) and the temperature profile in the growth region. At low  $S$ , the dodecahedra and the hexagonal plates are formed, while at higher supersaturation, the other crystal morphologies are formed. Halliday et al. [54] reported the crystallization of CdTe by a new multi-tube vapor growth technique at a temperature of 700°C. Photoluminescence studies were implemented to probe the distribution of impurities and defects through the crystals. Synthesis occurred at a low temperature (700°C) compared to the melting point (1090°C) to produce high-quality crystal with reduced defect density, but the critical resolved shear stress increases with decreasing temperature. Reduction in thermal strain and background contamination are also benefits of the reduced growth temperature. In addition, the CdTe phase diagram favors the synthesis of the stoichiometric sample through the intentional reduction of temperature. Crystal synthesis via sublimation is in the spotlight in the field of crystal growth technology because of the versatile characteristics like stoichiometric preparation of compound materials, less contamination, and no moving parts in the growth furnace. This method could be able to produce diverse crystalline habits (surface morphology) and growth patterns, having superior properties to other melt or solution that has grown counterparts. Large dimensional (15 cm<sup>3</sup>) CdTe single crystals are grown via the self-nucleation vapor method as reported by Grasza [55] but involving the translational movement of the ampoule along with the presence of hydrogen inside the tube. The grown crystals are found to be twinned in 30–80 vol% of the crystals and are oriented along the (110), (111), or (100) crystallographic direction. The pressure at which the vapor growth is performed inside the ampoule is 130 torr of hydrogen enclosed in a cold ampoule ensuring the reproducibility of the growth conditions and stable growth.

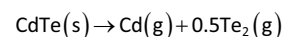
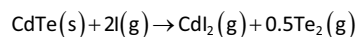
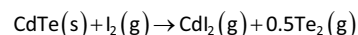
## 2) Chemical Vapor Transport (CVT) Method

Deposition of CdTe single crystals by employing the chemical vapor deposition in a closed tube arrangement is discussed in the literature

[56, 57]. Paorici et al. [58] reported the growth of CdTe crystals by chemical vapor transport and using NH<sub>4</sub>Cl as a transporting agent. The use of carrier gases may contaminate the crystal lattice because of that additional cleaning or polishing is essential to remove such impurities from the crystal surface. Grasza [55] synthesized crystals 3.5 cm in length and 5.5 cm in diameter under 130 torr hydrogen atmosphere by vapor growth method of self-nucleation and the growth was carried out in a non-contact mode between the crystal and ampoule wall. Paorici and Pelosi [59] discussed the CVT growth of CdTe semiconductor. The chemical route is outlined below:

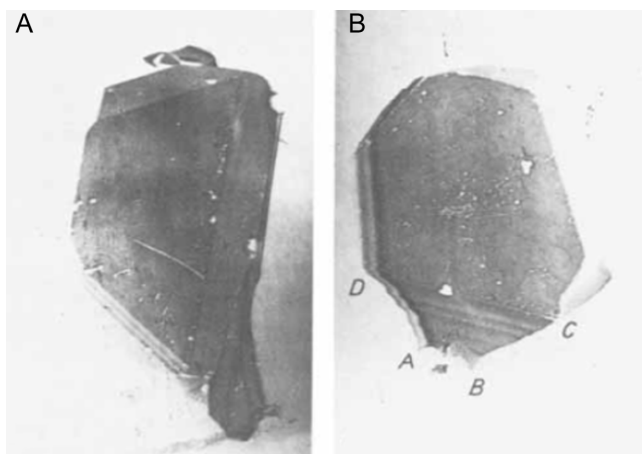


Where, X = Cl, Br, and I provided that the thermodynamic environment is selected so that the Te partial pressure is balanced below its saturated value. This could help to avoid the formation of melt–solid interface during the chemical transport process. In this case, the CdTe crystal is synthesized by solid–liquid–vapor technique. On the other hand, the carrier gases may incorporate into the lattice sites during the growth, which will badly affect the optoelectronic properties of the sample. Moreover, in the presence of a solid phase constituted by chemically homogeneous CdTe, three independent heterogeneous equilibria can be written as follows:



## 3) Horizontal Unseeded Vapor Growth Method

The horizontal unseeded method is one of the vapor growth methods for the bulk synthesis of crystals, in which CdTe precursors are uniformly distributed in a silica glass tube. The ampoule was etched with the help of HF and HNO<sub>3</sub> solution before filling the source materials to avoid extraneous impurities from the ampoule and later baked at 1000°C [60]. However, this growth method is suitable for the growth of good quality as well as a mirror-like CdTe crystal along with stoichiometry because carrier gases or seeds were not used for this vapor deposition process. But this growth method took a long time for the production of crystals (around 2 weeks) as discussed by Auleytner et al. [61]. The CdTe crystals harvested from this method



**Fig. 11.** CdTe crystals grown using horizontal vapor growth method [55].

are depicted in Fig. 11. Even though this crystal has some minute defects on the surface due to the over deposition of the atoms during the vapor growth, it has only a lower dislocation density than compared to the other melt or solution grown samples. Even though vapor growth is well known for the production of high-quality single crystals with diverse morphologies, the presence of structural defects in large single crystals of CdTe, non-stoichiometry, and the yield of small-sized crystals make this method inferior as compared to melt crystal growth [60].

### C. Solution Growth Method

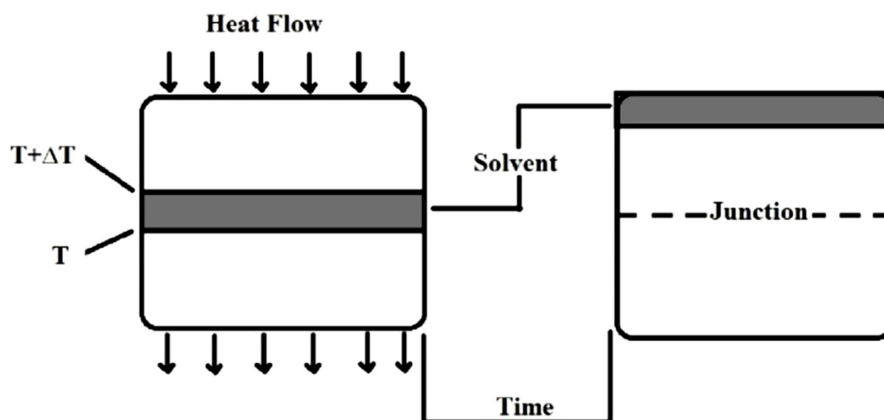
#### 1) Traveling Heater Method (THM)

For decades, THM has been the most popular form of traveling solvent technique because it combines zone melting and solution growth. In THM, a molten zone is allowed to transport the source material through the slow movement of the ampoule relative to the heater, as shown in Fig. 12. Taguchi et al. [2] have grown high-quality CdTe single crystals by the THM. However, THM synthesis protocols have some demerits. It is difficult to avoid contamination

from silica tubes and there is a high concentration of lattice defects during crystal growth at a temperature above the melting point. The inner pressure of the growth tube is precisely controlled by Te atoms, which are sufficiently supplied from the Te solution during crystal growth. The two emission bands from the energy range (1.42 and 1.10 eV) suggest that the grown crystals have Te vacancies, and 1.10 eV peak indicates the presence of imperfection. Taguchi et al. [2] have grown a high-purity CdTe single crystal from Te and  $\text{CdCl}_2$  solutions by THM. Because of its (a) lower contamination and (b) lower defect density, THM is one of the most suitable techniques to grow high-purity single crystals. The Te and  $\text{CdCl}_2$  are in the solution zone, which is melted with the help of a central resistance heater (as marked in Fig. 12). The furnace temperature is regulated to be high enough to dissolve the CdTe initial material to establish a concentration gradient. The zone-refined polycrystalline feed material dissolves into the hot solution region, diffuses down through the solution, and is deposited at the lower temperature region.

### VII. STRUCTURAL CHARACTERISTICS

The crystal structure and the quality of the unknown or known samples can be probed with the powder X-ray diffractometer. The growth method, internal and external structure, or the arrangement of atoms in the material will directly influence the physical properties. Shaaban et al. [62] discussed that the polycrystalline CdTe thin films have a zinc-blende (cubic) crystal structure. They also calculated the microstructure parameters, crystallite size, and microstrain and arrived at a conclusion that the crystalline size increases and microstrain decreases with film thicknesses. In the case of thin films, the peak intensity of the diffracted X-ray will increase with the film thickness, owing to the availability of the ordered atoms in the lattice points. In most of the optoelectronic applications, the researchers and the industries are looking for the single crystalline samples, because of the proper arrangement of atoms and bond strength which govern the performance of the device. While observing the peaks, we can be able to judge the crystallinity of the sample in a general manner. More broadness of the peak means lattice distortion or small particle size. Suppose the line width is small, it indicates good quality of the sample (proper arrangement of the atom along that direction). Careful determination of the planes and the



**Fig. 12.** Schematic depiction of the principle of traveling solvent method [2].

determination of the lattice parameters, density, cell volume, particle size, dislocation density, microstrain, etc. from the XRD data are enough to judge the crystal. The powder X-ray profiles of the CdTe single crystal and the powdered materials are presented in Fig. 9c. The right phase formation of the absorber material is inevitable for the fabrication of photovoltaic devices or any other electronic gadgets.

## VIII. OPTOELECTRONIC CHARACTERISTICS OF CDTE

### A. Optical Properties

Cadmium telluride single crystals have direct allowed band gap (1.43 eV). This allows the maximum absorption of photos from the sun light in a small thickness of the absorber than the indirect semiconducting materials like silicon and germanium. Even though CdTe has high toxicity and high melting temperature, the researchers are still behind this crystal due to the aforementioned reasons and its optimum electrical parameters for solar cell applications. The photoluminescence spectroscopy (PL) studies of the LPVB-grown CdTe crystals under a  $\text{SiCl}_4$  atmosphere at 0 and  $1.3 \times 10^3$  pa were conducted by Sekine et al. [12] and they reported the results obtained in both the atmosphere. Cadmium telluride crystals exhibit a sharp bound exciton peak at 1.59 eV, these peaks suggest the low carrier concentration. On the other hand, Halliday et al. [54] have grown CdTe single crystal through vapor growth method and measured the optical properties through PL analysis. Saha et al. [63] have reported the optical properties of the polycrystalline CdTe thin films deposited by direct method. The films were deposited at different thicknesses and the band gaps were measured. At 700 nm thickness of the film, the band gap was obtained as 1.56 eV. On the other hand, the less thickness films possess very high  $E_g$  ranging from 1.62 to 1.94 eV; the micro-strain of these sample are found to be very high than the 700 nm thick film. This result suggests that as the thickness enhances, the optical band gap also increases. The CdTe crystal exhibits direct nature of absorption; hence, this material will effectively absorb the solar radiation in the visible region. Also, the band gap and absorption coefficient are optimum for the solar cell application. The dependence of optical constants on the deposition conditions of the thin film crystals, as well as the nature of doping, has also been studied. Yamada [64] reported that the melt grown CdTe have band gap of 1.43 eV, but they observed that excess of Cd and Te vacancies are the predominant canters in the crystals. The deviation of optical band gap in the CdTe thin films from 1.48 to 1.53 eV was observed, which is due to the polycrystallinity or the confinement effect of the small grins in the film surface [63].

### B. Electrical Properties

In general, the optoelectronic properties are the fundamental pillars for the selection of absorber as well as window layer for the solar cells. For an efficient photovoltaic device, the electrical parameters should be high, that is, the mobility and carrier concentration. On the other hand, the resistivity of the active or transparent layer should be low in order to enhance the carrier movement without any scattering or recombination. Inoue et al. [1] have grown CdTe crystals through the Bridgman method from the melt (melting point =  $1090^\circ\text{C}$ ) at a pulling rate of 10 mm/h then the specimens were cut from single crystals of CdTe. However, the grown crystals have traces of Al, Si, Mg, and Ca elements. The CdTe crystals have *p*-type electrical conductivity, carrier concentrations ranging from  $10^{12}$  to  $10^{14}/\text{cm}^3$ , mobility varied from 50 to  $100 \text{ cm}^2/\text{V sec}$  and the resistivity was in the order of  $102\text{--}105 \Omega \text{ cm}$ . From the aforementioned results, it is clear that high mobility will enhance the collection efficiency of the carriers before it gets recombined. Also, the low resistivity reduces the scattering of the photogenerated carriers during the transport process in the solar cells. The uniform electrical resistivity in the order of  $10^9 \Omega \text{ cm}$  of the CdTe crystals is grown along the (100) crystallographic orientation by the vapor growth method [61]. To understand the electrical properties of the impure CdTe crystals, the Ge- and Sn-doped CdTe crystals were studied by Panchuk et al. [39]. The crystals were grown by the vertical and horizontal Bridgman method, respectively. The change in electrical properties like carrier mobility and density with respect to the extrinsic materials are presented in Table III. Numerous research efforts are going on the crystal growth to improve the quality of the final products to enhance the performance of the optoelectronic properties of the CdTe crystals. The carrier mobility of the CdTe crystal grown from  $\text{CdCl}_2$  solution is much higher than the melt grown as well as the doped crystals, clear from Tables II and III. On the other hand, the carrier density of the Bridgman and solution-grown crystals was observed to be in the same order, but the doped CdTe crystals had low carrier concentration than the pure. Yamada [64] has reported that the melt-grown CdTe crystals exhibit *p*-type electrical conductivity with high resistivity at the enhanced temperature. As we discussed earlier about the importance of mobility in the solar cells, the CdTe samples show Hall mobility of  $80 \text{ cm}^2/\text{V s}$ , which is matching well with the standard data as presented in Tables II and III.

### IX. DEFECTS

The structural defects, impurities, dislocations, etc., on the crystals surface adversely affect the photovoltaic performance of the device.

TABLE II.  
ELECTRICAL PROPERTIES AT ROOM TEMPERATURE IN INTRINSIC *P*-TYPE AND *N*-TYPE CDTE SINGLE CRYSTALS GROWN BY TRAVELING HEATER METHOD AND BRIDGMAN METHOD.

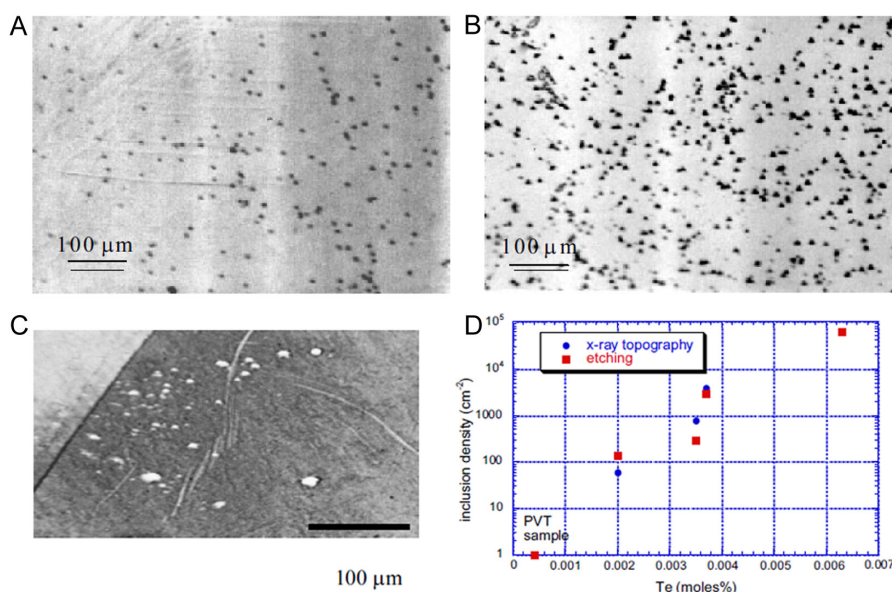
Growth Method	Conduction	Carrier Life Time ( $\mu\text{s}$ )	Carrier Density ( $\text{cm}^{-3}$ )	Carrier Mobility ( $\text{cm}^2/\text{V s}$ )
Te solution [29]	<i>p</i>	5.0	$8 \times 10^{12}$	96
$\text{CdCl}_2$ solution [29]	<i>n</i>	8.2	$1 \times 10^{16}$	1040
Bridgman–Stockbarger [29]	<i>p</i>	<0.8	$6 \times 10^{16}$	34
Bridgman grown [38]	<i>p</i>	--	$10^{12}\text{--}10^{14}$	50–100

**TABLE III.**  
ELECTRICAL PROPERTIES OF CDTE CRYSTALS + GE(SN) AT ROOM TEMPERATURE [32].

Growth Method	Conduction Type	Dopant	Carrier Concentration (cm <sup>-3</sup> )	Mobility (cm <sup>2</sup> /V s)
Bridgman method [34]	<i>P</i>	Ge	10 <sup>8</sup> –10 <sup>10</sup>	70
Bridgman method [34]	<i>P</i>	Ge	10 <sup>7</sup> –10 <sup>8</sup>	70–80
Bridgman method [34]	<i>N</i>	Sn	1.5 × 10 <sup>6</sup>	850
Bridgman method [34]	<i>n</i>	Sn	2.4 × 10 <sup>7</sup>	710
Bridgman method [34]	<i>n</i>	Sn	4.7 × 10 <sup>6</sup>	610

In this regard, the information/study with regard to the defect formation in CdTe crystal is important. The polycrystalline structure or defects formation like twins, grains, etc. in CdTe is due to the Te-cluster as reported by Fiederle et al. [38]. They also suggest that the superheating of these products will help to overcome the formation of multiple grains during the synthesis process. Shin et al. [21] detected the presence of Te precipitates in grown CdTe crystals using diverse tools such as Auger spectroscopy, X-ray diffraction, and Raman spectroscopy. The presence of precipitate may act as a scattering center during the transport process, which will deteriorate the device's performance. Later, many researchers reduced the Te defects by annealing in Cd over pressure at 600–800°C. This leads to an improvement of the infrared transmission due to Cd annealing. The low thermal conductivity (0.06 W/cm K) of the CdTe crystal near the MP is the next main source, for twins and grains. So, the thermal distribution of the CdTe source material is not homogeneous and the solidification from liquid to solid is not constant during the crystallization process. As we all know, in melt growth, the morphology of liquid–solid interface has a significant influence on the quality of the

crystals. Hence, the optimization of the interface is one of the major challenges in the field of the crystal engineering process to enhance the physical properties [47]. Several researchers employed dislocation studies to access the quality of the CdTe sample by a simple chemical etching method. On the other hand, both dislocation and inclusion density were dependent on the composition of the sample. Chemical etching is a facile chemical approach to unearth the nature and presence of dislocation on the crystal topography. During this, the solution or etchant may react with the crystal and remove the atoms or groups of atoms from the surface, if the atoms are arranged or bonded weakly. Both dislocation and inclusion density were dependent on the composition and the chemical bonding of the sample. Bissoli et al. [34] discussed the triangular-shaped etch pits on the CdTe single crystal. The micrographs of CdTe samples with different stoichiometry deviations are depicted in Fig. 13a-c. The variation of inclusion density with respect to the Te inclusion on the CdTe sample was graphically presented in Fig. 13d. On the other hand, the Bridgman grown crystals were chemically etched and the pits were found as spread in a cellular manner on the surface of the



**Fig. 13.** Etching micrographs of CdTe samples with different stoichiometry deviations: (a) 0.0035 at%; (b) 0.0063 at%; (c) Te inclusions in CdTe crystals, and (d) dependence of the inclusion density on the deviation of the sample [22].



sample. This shape as well as the arrangement of the etch pits is due to the glide and climb of dislocations induced by thermal gradient at high temperature as explained by McDeitt et al. [41]. Sabinina et al. [21] studied and reported two types of grain boundaries on the melt-grown CdTe crystals, that is, high-angle and low-angle misoriented grain boundaries. The first one having more than  $10^\circ$  of misorientation between the adjacent grains and the low-angle grain boundary having  $1^\circ$  of misorientation among the adjacent sub-grain. So, the second one will not affect the functional parameters much as compared to the high-angle grain boundary. The small-angle grain boundary can be detected using the transmission electron micrograph or scanning tunneling microscope. There is an argument that the dislocation in CdTe crystals is due to the condensation of point defects incorporated into the solid during its crystallization from the liquid state [39]. Hall and Vander Sande reported the relationship between deformation properties and the corresponding microstructural changes in CdTe crystals [40]. Fig. 14 shows the relationship between the shear stress ( $\tau$ ) and the shear strain ( $\gamma$ ) curve of CdTe crystals at different temperatures. As the temperature increased, the  $\tau$  was found to decrease and  $\gamma$  enhanced. This highlights the proper control of temperature during the experimental process. The dislocations, defects, and stacking faults have a deleterious effect on the performance of the crystals for any application. So, the defect-free crystals are the need of the hour to strengthen the fundamental research and device fabrication in diverse field. Oda et al. [32] reported the dislocation density of Bridgman grown CdTe which ranged from  $8 \times 10^3$  to  $2 \times 10^4 \text{ cm}^{-1}$ . It is interesting to point out that for any type of growth, the quality of the raw material is important, especially in the case of CdTe crystals, in which the low purity of the precursors leads to wetness in the ampoule. This is because of the sticking of the ingot material to the inner surface of the growth tube and the contamination from the ampoule, which further lead to the formation of cracks on both the ampoule as well as the crystal. The wetting is mainly due to the presence of oxygen both in CdO and  $\text{SiO}_2$ . At high temperature during the crystallization process, one reacts with another and produces oxide compounds such as  $\text{CdSiO}_3$ . This extrinsic compound formation is the fundamental reason behind the wetting of CdTe and the ampoule after the solidification process.

To overcome these intricacies, the source material is properly purified and also the ampoule is cleaned thoroughly followed by drying but even the atmosphere can contribute oxygen to Cd and Te during the crystallization process. The chemical homogeneity, defects, dislocations, inclusions, etc., have a profound influence on the physical properties as well as the performance of the crystals and device. Therefore, it is imperative to reduce or optimize the chemical impurities or faults, grain boundaries, etc., in CdTe crystals by selecting the appropriate synthesis method. The following sections deal with the doping technology in CdTe crystals and the photovoltaic performance of CdTe absorber material to date.

#### X. DOPING TECHNOLOGY IN CDTE CRYSTALS

The major constraints or challenges of the pure CdTe-based solar cell research is the achievement of a high hole density in the CdTe absorber layer by means of controlled acceptor doping. In this regard, Kranz et al. [61] discussed the effect of copper (Cu) doping on the resistivity of the CdTe layer on flexible glass slide, which is treated by  $\text{CdCl}_2$  solution. Doping a minute amount of Cu ( $0.8 \times 10^{15}$  atoms per  $\text{cm}^2$ ) into a  $5 \mu\text{m}$  thick CdTe layer drastically decreases the resistivity by the three orders of magnitude and also increases the hole density. This experimental outcome shows that the carrier hole density in the polycrystalline CdTe layers could be increased by the careful optimization concentration of the dopant. The controlled doping of Cu into the CdTe layer in the inverted heterojunction device structure by means of evaporation method and subsequent annealing treatment enables appreciable efficiencies up to 13.6%. The carrier density in the CdTe crystal can be altered by means of doping. This will help to tune the flow of current in the device (close circuit current), thereby enhancing the power conversion efficiency of the device. The first-principle calculations on the CdTe crystals suggest that Cu dopants can occupy the Cd atomic site acting as an acceptor, as well as the interstitial positions acting as a donor [66]. In situ arsenic (As) doping on the CdTe thin films by employing the metal organic chemical vapor deposition (MOCVD) method resulted in a high density of carriers,  $3 \times 10^{16} \text{ cm}^{-3}$ , as reported by Kartapou et al. [67]. Accordingly, the open-circuit voltage was increased but it became sensitive to interface recombination at the high concentration of arsenic.

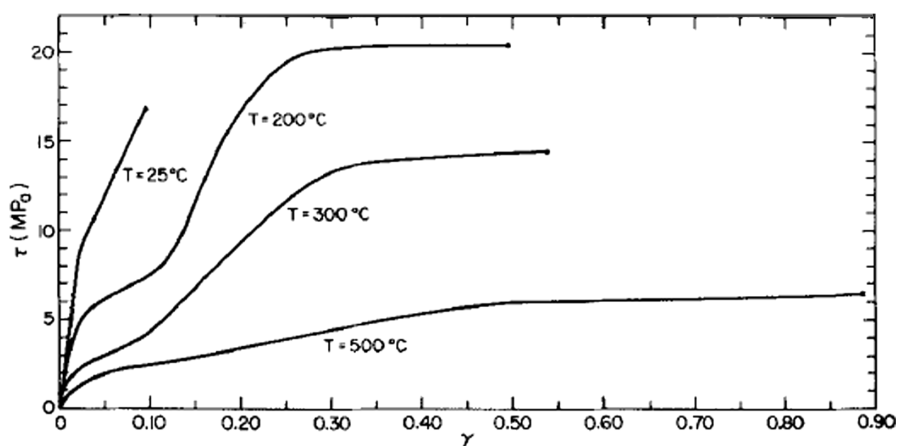


Fig. 14. Deformation behavior of CdTe single crystal [38].

## XI. APPLICATIONS

### A. Photovoltaic Performance

Competitions are still going on in the semiconductor industry on which absorber material will be able to overcome or rule over the elemental semiconductor silicon (Si) in the upcoming years. In this regard, drastic research is ongoing on compound semiconducting samples, especially on CdTe, GaAs, InP, etc. The GaAs materials are less attractive for the researchers because of the high toxicity problems, scarcity of the constituent elements (Ga and As), high melting temperature, and vapor pressure which facilitates complication in the growth of stoichiometric compounds. On the other hand, the CdTe solar cell reported a record cell efficiency of the order of 22.1% at the National Renewable Energy Laboratory (NREL), and the best commercial-size module efficiency is 11% [14]. The typical device structure of the CdTe solar cell includes a glass substrate, which is a transparent conducting oxide (TCO), *n*-CdS, *p*-CdTe, and finally a back conduct as reported by Halliday et al. [54]. This schematic diagram is presented in Fig. 1d. After Si-based solar cell, CdTe is the most popularly studied and well-understood material for solar cell fabrication. But still, there is a lack of a comprehensive data bank with regard to the functional parameters of CdTe crystals for energy harvesting applications. The basic knowledge of crystal, physical properties, and experimental protocols ease the fabrication of CdTe-based transistor as well as solar cell. Solar cell fabrication using CdTe crystals on the GaAs single-crystal substrates by MOCVD. Arsenic (As) and iodine (I) are used as dopants for *p*-type and *n*-type CdTe, respectively. On the other hand, the homo-junction solar cell structure was fabricated by growing *n*-type CdTe directly on bulk *p*-type CdTe single-crystal substrates as reported by Su et al. [68]. Fig. 15 shows the schematic depiction of a polycrystalline wafer with randomly arranged number of grains and a single-crystal CdTe wafer. The research team also reported that the short-circuit current of the homojunction solar cell is less than 10 mA/cm<sup>2</sup>. The open-circuit voltage of the device was 0.86 V. These results open up the possibility to enhance the efficacy of the CdTe solar cells as per the quality of source material like crystallinity, stoichiometry, thermal, mechanical, and optoelectronic properties.

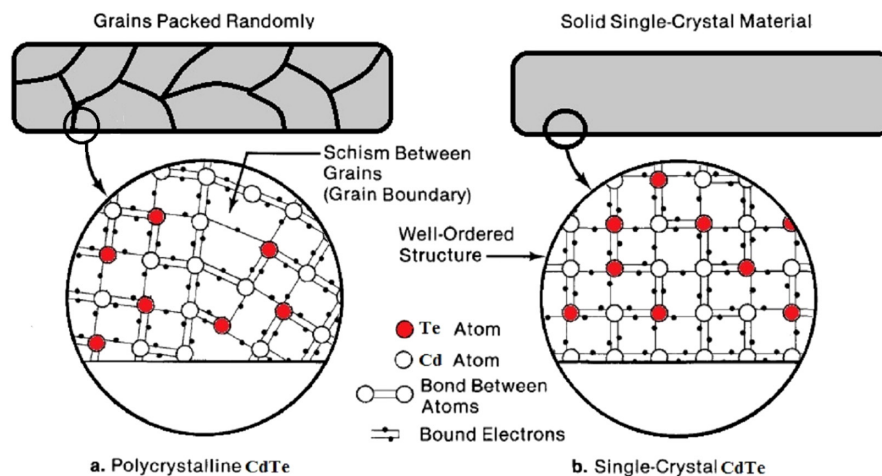


Fig. 15. Schematic depiction of the polycrystalline and single-crystalline CdTe crystals.

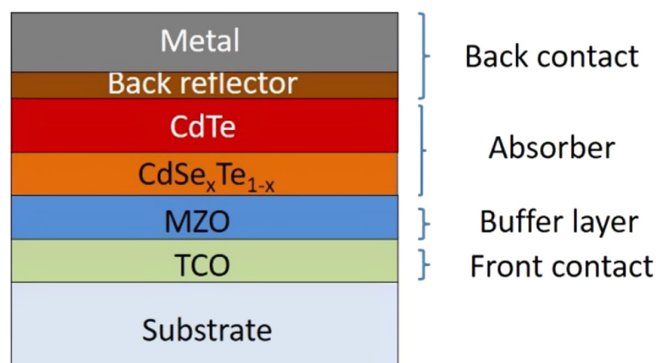


Fig. 16. Schematic depiction of the ITO/TCO/MZO/CdSe<sub>x</sub>Te<sub>1-x</sub>/CdTe/Back reflector/Metal device structure.

Romeo and Artegiani [69] reported that the CdTe solar cell has shown an improvement in the efficiency ( $\eta$ ) during the recent years due to the development of efficient back contact or back reflector, modification of bandgap by doping CdSe<sub>x</sub>Te<sub>1-x</sub> in the CdTe absorber, substitution of cadmium sulfide with MgZnO transparent buffer layer, and the novel redesign of the solar cell model (Fig. 16). For a very long time span, CdTe record efficiency had been kept constant at 16.7%, but recently, researches have reported that the CdTe single solar cell exhibited 22.1% and a module possesses 19% of efficiency [70]. Green et al. [71] demonstrated an efficiency of 15.8% on the CdTe-based solar cell. The sudden improvement in efficiency was obtained by a modified design of the CdTe solar cell device, elimination the of CdS buffer layer, considering new features such as bandgap grading using doping or the experimental protocols, copper incorporation into the lattice site of the CdTe crystals, and more transparent *n*-layer. These changes help the device to attain an efficiency of up to 21.5%, which later improved to 22.1% [72, 73]. The main reason behind these improved results has been gained from stoichiometric materials obtained from the production line. On the other hand, the open-circuit voltage value of this crystal is still below the elemental Si and GaAs absorber solar

cells. This is due to the large improvement of the current density ( $J_{sc}$ ), 30 mA/cm<sup>2</sup>, [71]. Fig. 16 shows the schematic model of the thin-film solar cell, which revolutionized the CdTe device structure and enhanced the  $J_{sc}$  and  $\eta$ . It is worthwhile to note that the comparison of quantum efficiency measurements of CdTe solar cells engineered using the CdSe buffer between CdS and CdTe by Paudel et al. [74] suggests that the enhancement in current density can be attributed to a specific fabrication of the heterojunctions. The introduction of CdSe increases the quantum efficiency response both in the blue (high energy) and in the long-wavelength region (825–930 nm). Therefore, the suitable mixing of the CdSe and CdTe layers by the activation treatment forms a photoactive CdSe<sub>x</sub>Te<sub>1-x</sub> compound, which has a narrower bandgap than pure CdTe; hence, lower-energy photons are also absorbed by this semiconductor. The introduction of a Se-doped CdTe compound with  $0.3 < x < 0.4$  reduces band gap of the absorber to approximately 1.4 eV. Moreover, when the CdS window layer is substituted with a more transparent MgZnO, it improves the band alignment with CdSe<sub>x</sub>Te<sub>1-x</sub> decreasing in carrier loss [75]. CdSe layer of 100 nm thickness by sputtering followed by CdTe by closed sublimation process achieved a suitable CdSe<sub>x</sub>Te<sub>1-x</sub> layer, recorded the current density of 29.8 mA/cm<sup>2</sup>, as reported by Baines et al. [76]. The Schottky-queisser limit predicts that the CdTe absorber-based solar cell has record efficiency of around 32%; however, this  $\eta$  will be very difficult to attain, considering the limitations of the polycrystalline junction as well as the efficiency loss for the industrial scale. An alternative approach developed to reach very high efficiencies in a relatively short time is to combine different band gaps together in order to optimize light absorption and energy conversion. Multijunction solar cells reach very high efficiency but they need high costs for production and result in a non-particularly advantageous efficiency/cost ratio. Recently, alternative tandem-structured solar cells were fabricated with silicon crystalline in order to obtain high efficiency [77]. In the last few years, researchers are trying to grow high-quality CdTe source materials in order to enhance device efficiency. Hence, the present review pens down on the deposition and growth of less-defect CdTe crystals, which will give more insight into the enhancement of photovoltaic device characteristics.

## XII. CONCLUSION

This review work focuses on the various technologies to grow bulk CdTe crystals through melt, vapor, and solution approaches. There is no single source of information regarding the diverse types of growth methods for stoichiometric crystallization. So, this work tries to shorten the researcher's gap in comprehensive knowledge about the synthesis protocols, phase diagram, structural parameters, optical properties, electrical properties, defect formation, and applications in CdTe compound semiconductors. In terms of physical properties, we mainly focused on the structural, optical, and electrical characteristics of the CdTe crystal and the diverse factors affecting its homogeneous growth. The presence of defects in the CdTe crystals during the growth and after the growth is reviewed and discussed in detail. Moreover, the doping technology and CdTe-based applications in the field of solar cells are briefly discussed at the end of the section. Hence, this review will satisfy the CdTe crystal researchers, because all the physical properties have been tabulated and the possible CdTe growth method has been discussed.

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## Appendix

The position of cadmium (Cd) and tellurium (Te) in the periodic table were highlighted in a thick black square box marked in Fig. S1. Cadmium is a silvery white colored soft metal with an atomic number 48. But, tellurium is a brittle and little toxic semimetallic element with an atomic number of 52.

Romeo and Artegiani [48] have reported tha the CdTe solar cell devices with superstrate configuration (see Fig. S2) are the best option in terms of efficiency, primarily because this structure allows the necessary post deposition treatment to be effective manner without any damage of the fabricated product. Generally, the window and absorber layers in cadmium telluride cells (CdS and CdTe) are grown on the front contact, which is a degenerately-doped semiconductor, typically an oxide layer, defined as transparent conducting oxides (TCO) like indium tin oxide (ITO) or fluorine-doped tin oxide (FTO). The supporting substrate is preferably a low-cost soda-lime glass when the deposition is obtained at substrate temperatures below 450°C (melting temperature of glass ~ 500°C), otherwise a more expensive alkali-free glass needs to be applied in case of high substrate temperature.

**Periodic Table of the Elements**

Fig. S1. Cd and Te were marked in the periodic table.

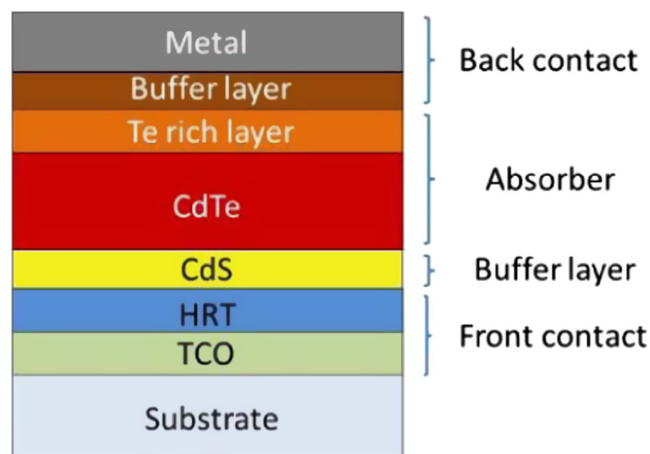


Fig. S2. Schematic of a standard superstrate CdTe based solar cell [54].