Growth of CdZnTe Crystals by Bridgman Technique with Controlled Overpressures of Cd

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Abstract. In this study, Cd1-xZnxTe crystals, with x = 0.20, were grown by closed-ampoule directional solidification (Bridgman) technique with a controlled Cd overpressure. Both unseeded and seeded growths were performed with total material charges up to 400g. After the loading of starting CdZnTe material, a typical amount of 2g of Cd was also loaded inside a Cd reservoir basket, which was attached beneath the seal-off cup. The ampoule was sealed off under a vacuum below 1x10^-5 Torr. The sealed ampoule was placed vertically inside a 4-zone Bridgman furnace - a Cd reservoir zone with a heat-pipe furnace liner on the top, followed by a hot zone, a booster heating zone and a cold zone at the bottom. The Cd-zone temperature settings ranged from 785 to 825°C. The growth process to consistently produce large grain, high crystalline quality CdZnTe was developed. Crystals of high electrical resistivity have been reproducibly obtained with In doping.

Introduction

The great advantages of CdZnTe as high-energy radiation detector are its high resistivity and large band gap, so that unlike other solid-state semiconductors such as silicon or germanium, CdZnTe can be operated at room temperature with energy resolution of only a few percent at 120 keV (see reviewed articles [1,2]). The capability for high-resolution spectroscopy and imaging studies without cryogenics, as well as in an energy range of significantly untapped potential, open the possibility of revolutionizing gamma-ray astronomy. In order to have reasonable detection efficiency at 600 keV, dense and high-Z detectors (such as CdZnTe) in the thickness range of 5 to 8mm are required.

CdZnTe is usually made by a high temperature melt growth process known as the Bridgman technique. The basic requirement of high resistivity needs the precise control of stoichiometry of the grown crystals. The crystal lattice structure of CdZnTe also has a natural tendency toward growth defects and non-uniformities that inhibit efficiency of charge collection when an external field is applied. This inevitably degrades the energy resolution and overall response uniformity, and it forces users to settle for rather thin (few mm) devices. Also, the expense of high purity raw materials, the typically low yield from the growth process from poor quality ingots, and the need to attach complicated electrode structures to compensate for volume and surface effects on charge collection and noise, make the unit cost of CdZnTe detectors extremely high.

One of the most critical requirements for CdZnTe in the application of room temperature high-energy radiation detector is high electrical resistivity. This is paramount in order to reduce the bulk leakage current to an acceptable level. The high resistivity can only be achieved with materials of low carrier concentrations, which are controlled by the concentrations of intrinsic defects, i.e., native point defects such as Cd vacancy, and extrinsic point defects, including intentional and unintentional dopants. In this study, we have applied the known information on the solidus points and their equilibrium vapor pressures by growing crystals under controlled Cd partial pressures to control the stoichiometry, or the native point defect concentration, in the grown crystals.
Thermodynamic and Stoichiometry of $\text{Cd}_{0.80}\text{Zn}_{0.20}\text{Te}$

As a part of our initial investigation, we have performed the partial pressure measurements by optical absorption technique and established the corresponding $x_{\text{Te}}-T-P_{\text{Te}}$ data on the Te-rich solidus for $\text{Cd}_{0.80}\text{Zn}_{0.20}\text{Te}$ [3]. The so-called three-phase-loop of the partial pressure of $\text{Te}_2$ and Cd is shown in Figure 1(a) and (b), respectively.

![Figure 1](image-url)

(a)

Figure 1. The three-phase-loop of the partial pressure of (a) $\text{Te}_2$ and (b) Cd in equilibrium with $\text{Cd}_{0.80}\text{Zn}_{0.20}\text{Te}$
As shown in the figure, the partial pressures of Te$_2$ and Cd over the melt at the growth temperature (1145°C) differ by 3 orders of magnitude, i.e. $2 \times 10^{-3}$ atm for Te$_2$ and 1.8 atm for Cd. Hence, an initially stoichiometric charge will become Te-rich during growth because more Cd is lost to the free volume. From the vapor pressure of pure Cd, as shown in Figure 1(b), a Cd reservoir of 818°C will provide the necessary Cd pressure, i.e. 1.8 atm, in the vapor phase and maintain the melt at stoichiometry.

**Crystal Growth by Directional Solidification of Bridgman Technique**

**Homogenization of starting material.** The starting elements of Cd, Zn, and Te were high purity; either six-nines grade from Johnson Matthey or seven-nines grade from 5N Plus. The weighed elements were loaded inside fused silica ampoules, which have been previously cleaned and baked out under vacuum. The loaded homogenization ampoules were evacuated and sealed under vacuum condition. One pass of a heated zone was applied to the sealed ampoules, with the zone maximum at 520°C and a translation rate about 1cm/h, to ignite Te-rich eutectic exothermic reaction of the elements. Then, the ampoules were heated up under a vacuum of $10^{-3}$ Torr in a rocking furnace to 1070°C, soaked for 36h, raised temperature to 1160°C, rocked for 3 to 5 h before casting by turning off the furnace power.

**Crystal Growth.** The homogenization ampoules were opened and the starting materials were ground into the dimension less than 5mm. The growth ampoule was made of fused silicas with inner diameter from 20 to 40mm and a tapered length of 2.5cm at the growth tip. The cleaned ampoules were baked at 1180°C under vacuum condition for 16h. After the specific amount of the starting material was loaded inside the growth ampoule, a basket holding about 2g of pure Cd was inserted on the top of the ampoule as the Cd reservoir, which was attached beneath the seal-off cup. The ampoules were then sealed under a vacuum lower than $10^{-5}$ Torr. So far, about forty Cd$_{0.80}$Zn$_{0.20}$Te crystals have been grown using directional solidification by the Bridgman technique. A typical thermal profile and the initial ampoule position are shown schematically in Figure 2.

**Figure 2.** The thermal profile and the initial ampoule position for a typical crystal growth. Three thermocouples, represented by three different symbols were used for profiling.
Figure 2 shows that the ampoule is 32 cm long and the starting material is about 7 cm long. The thermal profile was provided by a 4-zone furnace, i.e. the top Cd reservoir zone which was equipped with a heat pipe (the isothermal furnace liner), the hot zone, the booster zone and the cold zone at the bottom. In order to make the starting melt maintaining above the melting point of 1130°C with a positive thermal gradient and a Cd reservoir which can be independently controlled at about 818°C, the Cd reservoir has to be located on the top of the 32 cm long ampoule. The range of the Cd reservoir temperature employed was from 750 to 935°C, with the range of 785 to 820°C for most of the runs. Both unseeded and ZnTe seeded growth ampoules were processed. The ampoule sizes were either 20 mm ID (25 mm OD) or 40 mm ID (45 mm OD). The typical translation rates were 0.75 to 2 mm/h. After the translation was completed the sample and the Cd reservoir were cooled down to room temperature over a period of 96 to 144 hours. However, the electrical property of undoped grown crystals was not consistent, even with the controlled Cd overpressure, with the electrical resistivity, \( \rho \), varied from \( 10^3 \) to \( 10^{10} \) Ω cm. By adding the intentional Indium dopant, 4 to 6 ppm, atomic, to the pure elements during homogenization, the electrical resistivity of the samples were consistently above \( 10^8 \) Ω cm when the Cd reservoir was between 785 and \( 825^\circ \)C.

**Characterization**

The grown crystals were retrieved by opening the ampoules. Usually, high crystalline quality boules were grown from very clean ampoules and starting materials, which can be indicated as the grown ingots slid inside the ampoule without any wetting to the ampoule wall. By experimenting with various growth parameters, single crystals have been consistently produced on the first 70% of a 20 mm diameter ingot as shown in Figure 3 below.

![Figure 3](image.png)

Figure 3. (a) A single grain of 4 cm in a 6 cm long ingot. (b) Single grain on the surfaces of three cuts along another grown boule.

For the larger diameter (40 mm) ingots, the crystals usually consisted of two major grains for the first 70% of the ingots. Twinning was observed to be confined in the shoulder region of the first grown section. Occasionally, completely twin-free ingots were grown, as shown in Figure 4, and the causes are being studied.

Hall measurements were performed on the as-grown samples and the measured resistivity for the In doped samples are consistently higher than \( 10^8 \) Ω cm. Two quantities, electrical resistivity and Hall coefficient, were measured. The measured values of resistivity and Hall coefficient are determined by four material parameters, namely, electron concentration, \( n \), hole concentration, \( p \), electron mobility, \( \mu_n \), and hole mobility, \( \mu_p \). The governing equation for resistivity, \( \rho \), is given by

\[
\rho = \frac{1}{ne\mu_n + pe\mu_p},
\]

and the equation for Hall coefficient, \( R_H \), under the condition \( \mu_n \gg \mu_p \) (as is the case in CdZnTe) can be expressed as:
\[ n = \frac{1}{\rho e \mu_n} \left( \frac{\mu_p}{\rho \mu_n} - R_{\mu} \right). \]  

To derive the individual values of electron and hole concentrations from eqs. (1) and (2), the experimental values of 1000 and 100 cm$^2$/Vs for the electron and hole mobility, respectively, published in the literature [4] for Cd$_{0.80}$Zn$_{0.20}$Te at room temperature, were used. Table 1 lists the measured Hall coefficients and resistivity at room temperature, and the derived electron and hole concentrations from two grown ingots, CZT-26 and CZT-29; both were doped with 4.2 ppm, atomic In and grown with a Cd reservoir at 785°C.

**Table 1.** The measured Hall coefficients and resistivity, \( \rho \), at room temperature, and the derived electron and hole concentrations, \( n \) and \( p \), from two grown ingots, CZT-26 and CZT-29. (CZT-29a and CZT29b were samples cut from different locations of the boule CZT-29)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hall coeff. [cm$^3$/C]</th>
<th>( \rho ) [( \Omega ) cm]</th>
<th>( n ) [cm$^{-3}$]</th>
<th>( p ) [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZT-26</td>
<td>8.9x10$^9$</td>
<td>2.1x10$^9$</td>
<td>3x10$^5$</td>
<td>2.8x10$^6$</td>
</tr>
<tr>
<td>CZT-29a</td>
<td>-1.84x10$^{13}$</td>
<td>8.4x10$^7$</td>
<td>~1.7x10$^6$</td>
<td>&lt;10$^6$</td>
</tr>
<tr>
<td>CZT-29b</td>
<td>-1.2x10$^{11}$</td>
<td>1.2x10$^7$</td>
<td>1x10$^6$</td>
<td>4x10$^7$</td>
</tr>
</tbody>
</table>

**Summary**

High resistivity CdZnTe crystals were consistently grown using In dopant concentration of 4 to 6 ppm, atomic and by controlling the Cd reservoir between 785 - 825°C as suggested by the established thermodynamic properties and information on stoichiometry of the Cd$_{0.80}$Zn$_{0.20}$Te system. The growth process to consistently produce large grain and high crystalline quality crystals of CdZnTe was developed.

The future work will be focused on the improvement on the yield of high resistivity and high crystalline quality single crystal CdZnTe boules by scaling the diameter up to 70mm and the further optimization of the furnace thermal profiles, ampoule design, growth and cooling procedures.

**References**

