CHARACTERIZATION OF CdZnTe SINGLE CRYSTALS GROWN UNDER DIFFERENT CADMIUM OVERPRESSURES

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OUTLINE

- Motivation
- Formation of Te inclusions/precipitate
- Crystal Growth of CdZnTe
- Synchrotron X-ray Topography Technique
- Correlation between synchrotron white beam X-ray topography (SXRT) and transmission infrared microscopy
- Effect of Cd reservoir temperature on Te inclusion density
- Summary
CdZnTe has gradually become a choice material for radiation detectors due to its:

- Direct wide band gap (1.5-2.3 eV) ⇒ High bulk resistivity
- Large cross-section ⇒ Good photoelectric absorption
- High energy resolution comparable to high quality Ge (0.5% at 662 keV) and high spatial resolution (~µm) for imaging
- Ability to operate at room temperature ⇒ no cooling required

**Current CdZnTe Applications include**

- National security (nuclear waste management, nonproliferation of nuclear materials,...)
- Medical imaging (PET and CT scanners, medical probes,...)
- Basic science (astrophysics, γ-spectrometer, synchrotron X-ray research,...)
- Industrial imaging (X-ray and γ-ray cameras,...)
- Electro-optic modulators and laser windows

### Comparison of CdZnTe with detector materials

<table>
<thead>
<tr>
<th></th>
<th>CdZnTe</th>
<th>Ge</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average atomic #</td>
<td>49.1</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td>Density (g/cm3)</td>
<td>5.78</td>
<td>5.32</td>
<td>2.33</td>
</tr>
<tr>
<td>Resistivity (W-cm)</td>
<td>$10^{10}$</td>
<td>47</td>
<td>$2.3 \times 10^5$</td>
</tr>
</tbody>
</table>

**bone densitometer**

http://www.megamedicals.com/mm-x010-bone-densitometry.htm

**Miniaturized probe for radioguided surgery**

FORMATION OF Te INCLUSION/PRECIPITATES

- Te precipitates (~nm order) form from the retrograde solid solubility effect in CdZnTe during rapid cooling from high temperature, whereas Te inclusions (~µm order) result from trapping of the excess Te at growth interface because of fluctuation in growth conditions (e.g. temperature, pressure).
- These secondary phases (Te inclusions/precipitates) reduce infrared transmission and also affect detector performance (e.g. by reducing carrier lifetime).

⇒ How to inhibit/prevent the formation of these secondary phase Te particles???

⇒⇒ A proposed solution is to use saturated Cd vapor pressure!!!

Partial pressures of Te$_2$ (left) and Cd (right) for four samples of Cd$_{0.8}$Zn$_{0.2}$Te with different Te contents have been measured [1].

One implication from the partial pressure measurements is that the partial pressures of Te$_2$ and Cd over the melt at growth temperature (1150°C) differ by 3 orders of magnitude. Therefore, an initially stoichiometric sample will be Te-rich during growth because more Cd is lost to the free volume. A Cd reservoir of 818°C will provide the Cd in the vapor phase and maintain the melt at stoichiometry.

The homogeneity range of Cd$_{0.8}$Zn$_{0.2}$Te solid solution determined from partial pressure measurements. Solid squares are the solubility limits at Te-saturated condition. The maximum limit is less than 0.50016. There are no data points on the Cd-rich region and dotted line is arbitrarily drew.

The thermal profile and the initial ampoule position for a typical crystal growth by vertical directional solidification with controlled Cd over-pressure.
CdZnTe boules were grown by vertical directional solidification method, and subjected to different Cd overpressures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Start material</th>
<th>T (°C) Cd reservoir</th>
<th>Growth time (hr)</th>
<th>Sample cooling time (hr)</th>
<th>Cd reservoir cooling rate during growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>2G-30</td>
<td>Batch #2</td>
<td>785</td>
<td>120</td>
<td>144</td>
<td>80°C in last 60 hr</td>
</tr>
<tr>
<td>2G-31</td>
<td>Batch #2</td>
<td>800</td>
<td>125</td>
<td>96</td>
<td>65°C in last 60 hr, quenching sample when at 480°C</td>
</tr>
<tr>
<td>2G-34</td>
<td>Batch #7 (no In dopant)</td>
<td>840-845</td>
<td>125 (1.2 mm/hr)</td>
<td>96</td>
<td>60°C in 60 hr</td>
</tr>
<tr>
<td>2G-36</td>
<td>Batch #8</td>
<td>785</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2G-38</td>
<td>Batch #9</td>
<td>810</td>
<td>125 (1.2 mm/hr)</td>
<td>96</td>
<td>60°C in 75 hr</td>
</tr>
</tbody>
</table>

[Vertical Bridgmann Technique diagram](http://alineason.com/index.php/en/knowhow/crystal-growth)
SYNCHROTRON X-RAY TOPOGRAPHY (SXRT)

(a) Beam shutter X-ray beam Storage ring
sample X-ray beam ~ 25 m Storage ring

(b) Beam shutter Si monochromator Storage ring
sample X-ray beam ~ 50 m Storage ring

NSLS X19C
White spectrum

APS 1-BM
Monochromatic

Transmission
Back-reflection
Grazing-incidence
**Orientation contrast**

Origin: misorientation leads to either the absence of diffracted beam or the overlapping/separation of diffracted beams, thus creating contrast.

**Extinction contrast**

- Direct image ($\mu t < 1\text{-}2$): waves diffracted from distorted region kinematically does not undergo primary extinction, thus having higher intensities than the waves from perfect regions.

- Intermediary image ($\mu t \sim 2\text{-}4$): new wavefields created at defect surface interference with original propagating wavefield creating fringe type contrast.

- Dynamic image ($\mu t > 5$): under high absorption condition, a small amount of deviation from the exact Bragg’s condition will result in waves from branch 1 suffering much more absorption, leading to a white contrast.
CORRELATION BETWEEN SYNCHROTRON WHITE BEAM X-RAY TOPOGRAPHY AND INFRARED MICROSCOPY
Pictures of a 38mm diameter grown crystal: (a) as-grown crystal slid inside ampoule (b) twins were observed at the tip shoulder (c) two grains were nucleated at the tip (d) two grains on a cutting surface with the major gain covers about 70% of the area.
Sample CZT-36/1 was cut from CZT-36

Reflection SXRT shows sample consists of two grain of relatively high crystallinity

Network of subgrain boundaries and dislocation dominate the microstructure of the sample

No precipitates are resolved on the topographs

No slip bands or twins observed

Relative lattice distortion near certain region along periphery most likely due to contact with ampoule walls
Left: Transmission infrared micrograph of CZT-36/1 showing crack, and a bed of Te inclusions inside a boundary.
Right: Magnified I.R image of a section of Te filled boundary.
For each sample, left image is reflection SXRT of the whole sample, and right image is I.R micrograph of the sample.

- Reflection SXRT reveals network of subgrain boundaries dominate the microstructure of samples.
- Presence of inhomogeneous strain near edge of the samples.
- $G_1$ in sample 2G-30 display the largest amount of strain.
- I.R shows samples contains microcrack, which is can also cause the lattice distortion observed in the SXRT images.
Sample 2G-36 @ 785°C

Both transmission and reflection indicate a single crystal, with a network of subgrain boundaries.

Lattice distortion near edges of sample due to inhomogeneous strain.

I.R shows uniform distribution of Te inclusions smaller than 20μm.

Sample 2G-36

Sample 2G-38 @ 810°C

Reflection SXRT shows a highly distorted image due to large inhomogeneous strain.

I.R reveals the presence of microcrack, which also contributes to the lattice distortion observed in the SXRT images.
Enlarged I.R images showing size and shape of Te inclusions

Sample 2G-30 @ 785°C

Sample 2G-31 @ 800°C

Sample 2G-34 @ 840-845°C

Sample 2G-38 @ 810°C
EFFECT OF Cd RESERVOIR TEMPERATURE ON Te INCLUSIONS
Cd reservoir temperature at 717°C

747°C

754°C

800°C
Lowest amount of precipitates were obtained with Cd reservoir temperature at 815±15°C (comparing to 818°C predicted by partial pressure data for stoichiometric melt)
<table>
<thead>
<tr>
<th>Sample #</th>
<th>Cd reservoir (°C)</th>
<th>Cd reservoir cooling rate</th>
<th>Twinning</th>
<th>Strain</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2G-30</td>
<td>785</td>
<td>80°C in last 60hr</td>
<td>none</td>
<td>Severe lattice distortion near the edges, particularly in G₁</td>
<td>Consists of 2 grains, with G₁ showing a cellular microstructure and lattice distortion toward the edge</td>
</tr>
<tr>
<td>2G-31</td>
<td>800</td>
<td>65°C in last 60hr, quenching sample when sample at 480°C</td>
<td>none</td>
<td>Relatively small strain in main grain, with several highly distorted small grains</td>
<td>Single grain dominated by subgrain boundaries, and high density of dislocations.</td>
</tr>
<tr>
<td>2G-34</td>
<td>840-845</td>
<td>60°C in 60hr</td>
<td>none</td>
<td>Large distortion</td>
<td>Single grain, with relatively low strain dominated by subgrain boundaries and dislocation</td>
</tr>
<tr>
<td>2G-36</td>
<td>785</td>
<td>none</td>
<td>None</td>
<td>Very small strain near the edge</td>
<td>Single grain of good crystalline quality subgrain boundaries and low density of dislocation</td>
</tr>
<tr>
<td>2G-38</td>
<td>810</td>
<td>60°C in 75hr</td>
<td>none</td>
<td>Severe distortion due to large inhomogeneous strain</td>
<td>Single grain dominated by large inhomogeneous strain</td>
</tr>
</tbody>
</table>
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