BNL-90242-2009-CP

SNM Movement Detection/Radiation Sensors and Advanced Materials Portfolio Review
Novel Method for Growing Te-Inclusion-Free CdZnTe Crystals

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Presented at the RadSensing 2009 Conference
PNNL, Richland, WA
June 2-4, 2009

June 2009

Nonproliferation and National Security Department

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RadSensing2009

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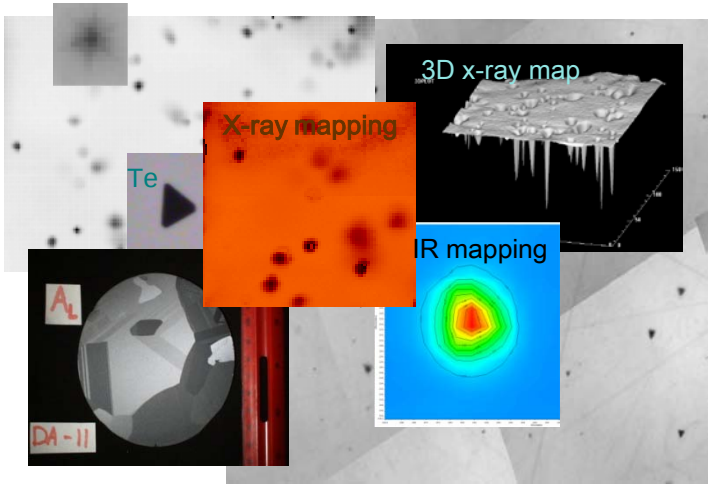
BNL

Research Team



Project started April 2008 (Month 14)

Budget: FY08 - $457K
FY09 - $450K
FY10 - $455K

- Dr. Ralph James, PI
- **Dr. KiHyun Kim, CZT Bridgman growth; 10 years experience with Bridgman growth of CZT and CMT; Joined 12/2008;**
- **Dr. Genda Gu, CZT Floating Zone Growth, 15 years experience with floating-zone crystal growth, including growth of CZT and CdTe;**
- **Ms. Veronica Carcelen, CZT Bridgman growth; 5 years experience with CZT and CdTe crystal growth;**
- Dr. Aleksey Bolotnikov, Detector Testing;
- Dr. Anwar Hossain, Detector Fabrication;
- Mr. Giuseppe Camarda, High-resolution Mapping of CZT;
- Dr. Ge Yang, Infrared transmission microscopy and thermal annealing of CZT;
- Mr. Stephen Babaloa, Infrared transmission microscopy to quantify Te inclusions/precipitates;
- Ms. Rubi Gul, Characterization of point defects using transient current spectroscopy and optically-induced DLTS;
- **Dr. Longxia Li, Consultant, 40 years experience with growth of CZT.**

Project Goal and Principal Aims

Goal: Find an improved growth method that will reduce, or possibly eliminate, the presence of large Te-rich secondary phases in CZT crystals, ultimately to increase the availability of spectrometer-grade crystals for nonproliferation applications

Aim 1. Use existing floating-zone growth facility to mix melt by rotation and measure effects on inclusion formation

Aim 2. Get new Bridgman growth furnaces and related lab equipment in place and operational, and complete initial tests of inverted growth concept

Aim 3. Conduct systematic crystal growth experiments, followed by development of synthesis and purification methods

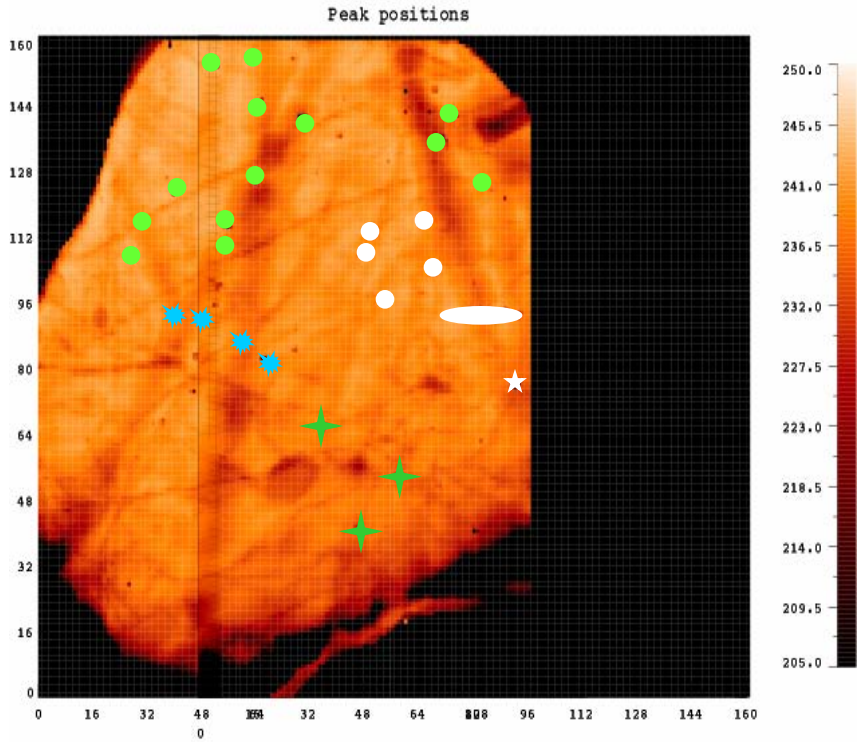
Aim 4. Conduct post-growth annealing studies to eliminate inclusions and precipitates and understand their origin

Aim 5. Perform material and device characterization for BNL-grown CZT

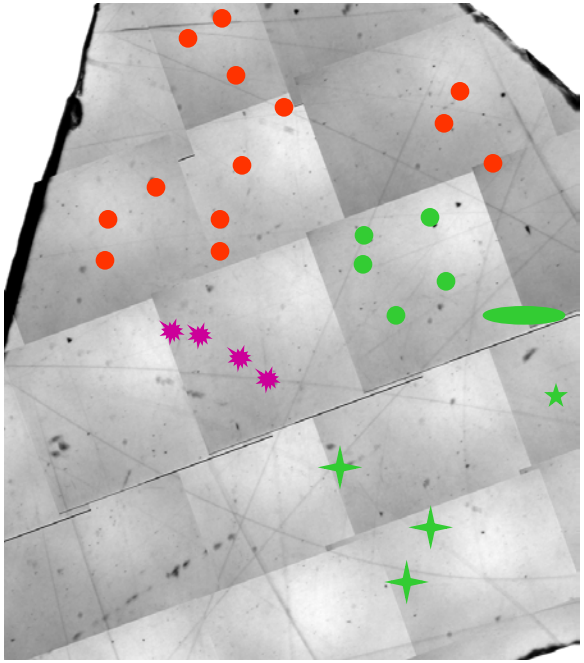
Aim 6. Dissemination of data

Correlations between x-ray map & IR image

X-ray map shows the degraded regions precisely correspond to Te inclusions on the right



IR image shows Te inclusions, which could be identified by composition and shape



Very high correlation found for all CZT samples.

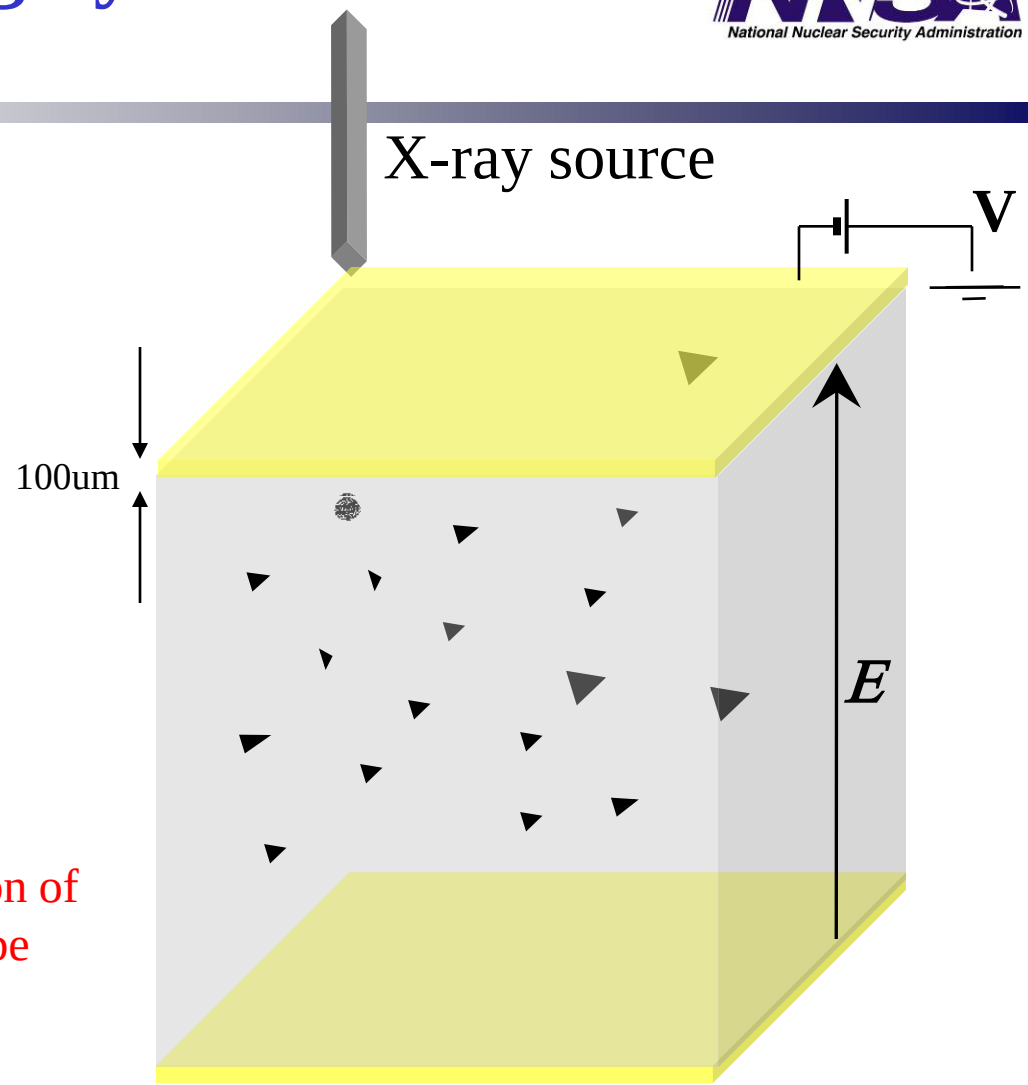
Electron trapping by Te inclusions

Assuming no other defects (such as cracks, grain boundaries, and twins) are present.

Charge trapped by an individual inclusion:

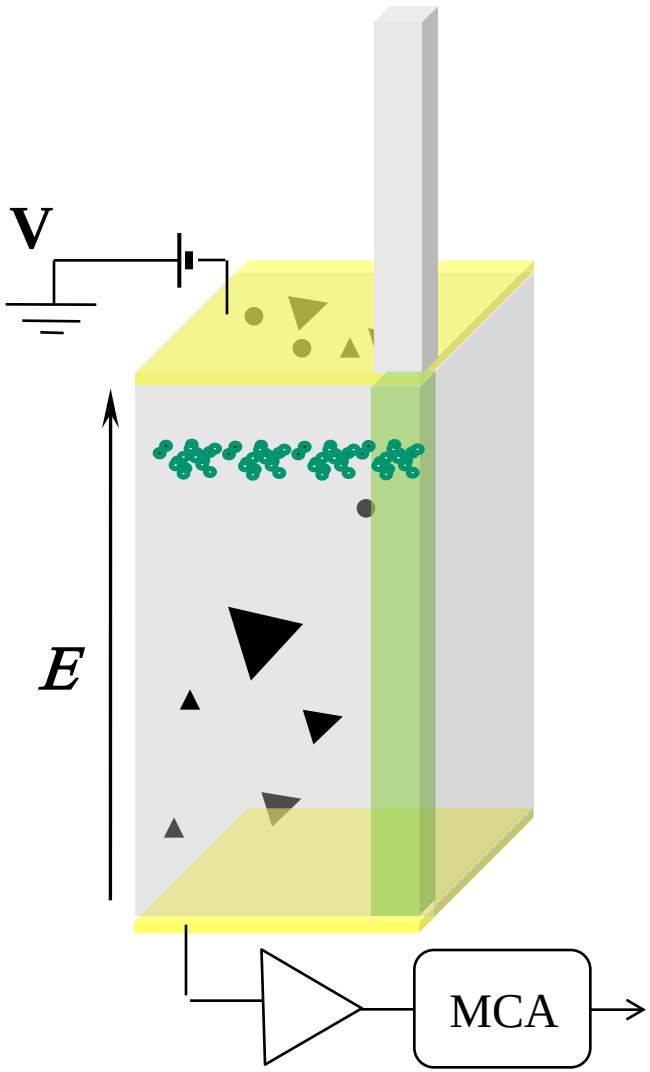
$$Q = Q_i\left(1-\eta_i\left[1-\exp\left(-\frac{D_i}{E_i\mu_i\tau_i}\right)\right]\right)$$

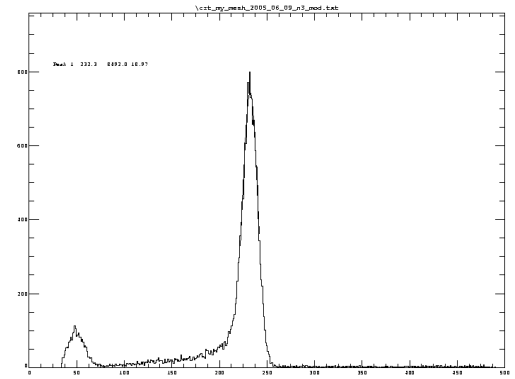
Many electrons are trapped per interaction. Stochastic process due to random distribution of Te inclusions => these fluctuations cannot be corrected!



CZT detector

Energy Spectrum with NSLS X-ray beam

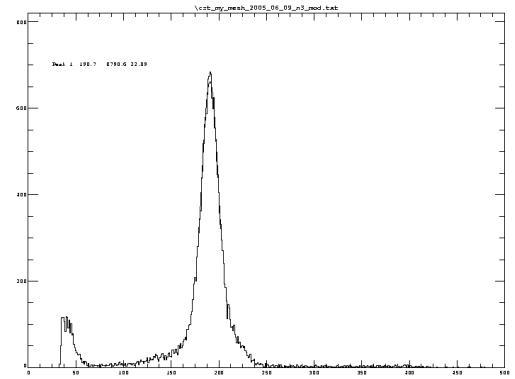




Full charge collection:

Photopeak at channel 480:

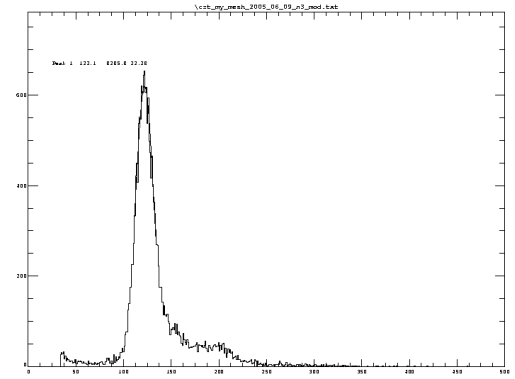
No defect in electron cloud's path.



Some charge is trapped:

Photopeak at channel 350:

Small defect in cloud's path.

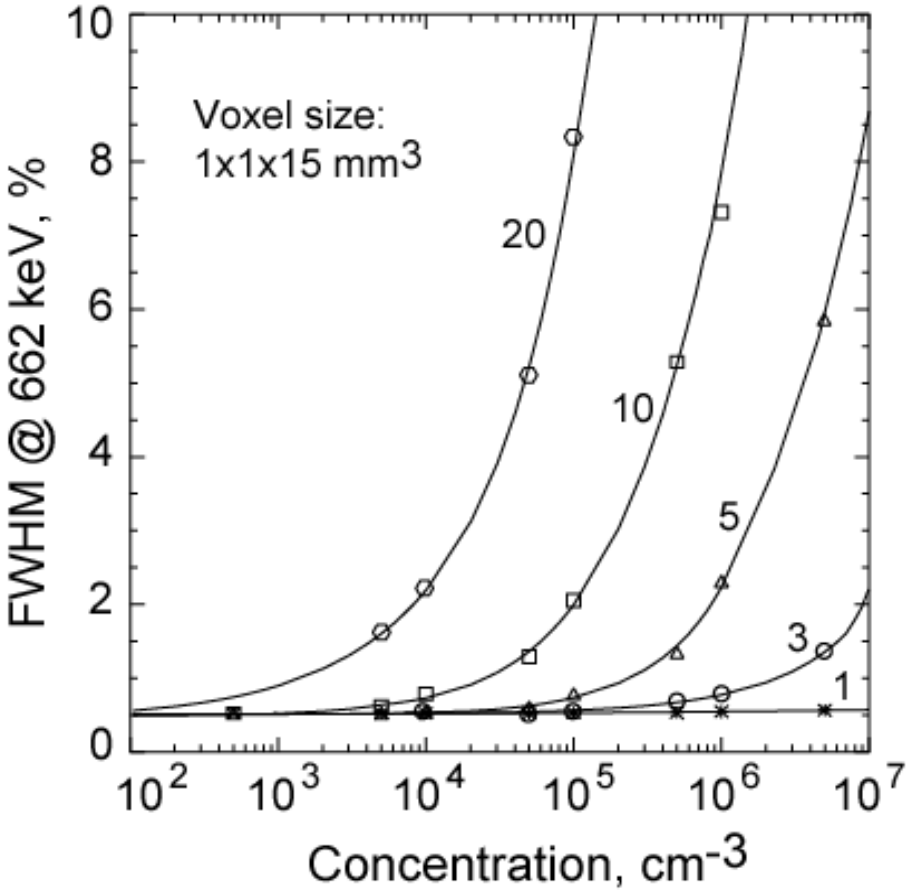


More charge is trapped:

Photopeak at channel 150:

Large defect in cloud's path.

Research establishes limits on number and size of Te inclusions for high-resolution detectors



Example: FWHM of photopeak vs. size (1-20 μm diameter) and concentration of Te inclusions.

The plots are calculated for a 1x1x15 mm^3 voxel for a single-carrier device irradiated with a ^{137}Cs source.

Electric field is 2000 V/cm.

Simulations predict that Te inclusions with sizes of < 2 μm behave as ordinary traps and can be tolerated.

Results confirmed by measurements!

Future thrusts for CZT detector technology: Improved growth methods and annealing

Goal: Reduce the size and concentration of Te inclusions in CZT crystals without adversely affecting the electrical resistivity or mobility-lifetime product for electrons

Approach: Perform new growth experiments and couple with mapping of device non-uniformity and 3-D distribution of Te-rich inclusions/precipitates

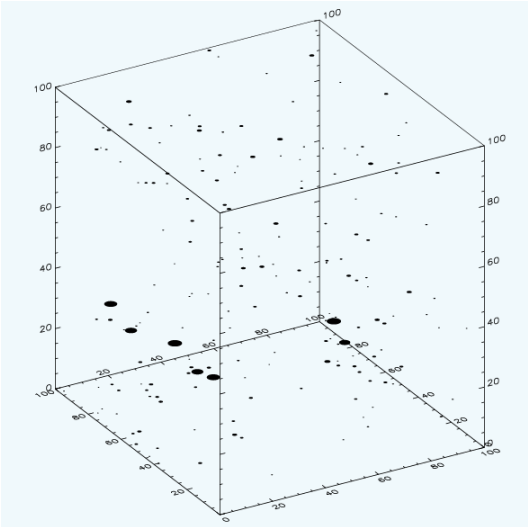
- Better mixing of the melt by rotation, magnetic stirring, or other means
- Modify design of ampoule (e.g., shape and closed systems) and of heating elements
- Reduce amount of excess Te in source materials
- Lower growth temperatures to reduce Cd loss
- Reduce Cd loss during growth and cool-down, including use of gas over-pressures
- Post-growth thermal annealing in Cd (or CdZn alloy) vapor

Hypothesis #1: *Large Te-rich secondary phases are caused by inclusions during growth*

Two Definitions:

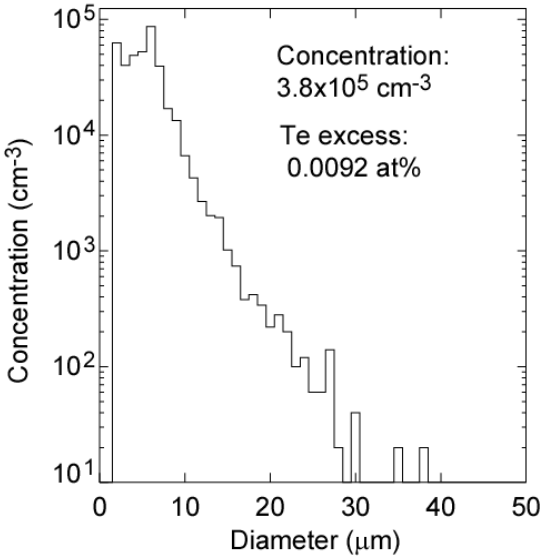
- The term “inclusion” describes any volume of material trapped inside a crystal during its formation.

- The term “Te precipitate” describes the coalescence of cadmium vacancies due to the limited solid solubility of Te in CZT.



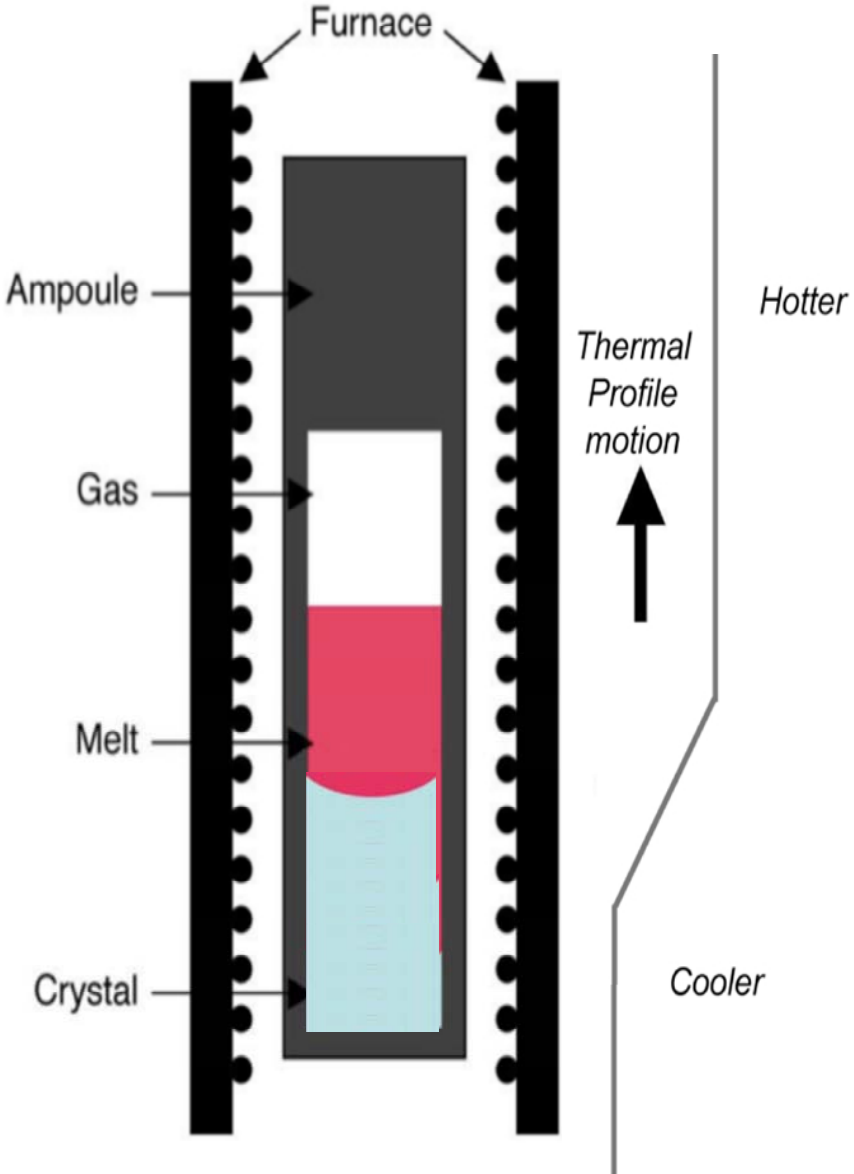
Te inclusions represented by dark discs

1x1x1 mm^3



Size distribution of Te inclusions

Hypothesis #2: *Te inclusions are formed by encapsulation of Te-rich droplets in the melt*

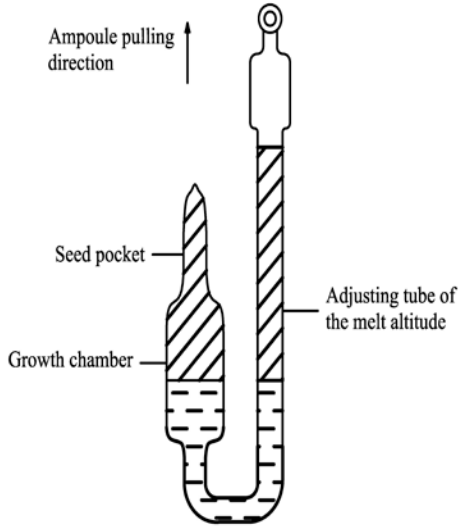


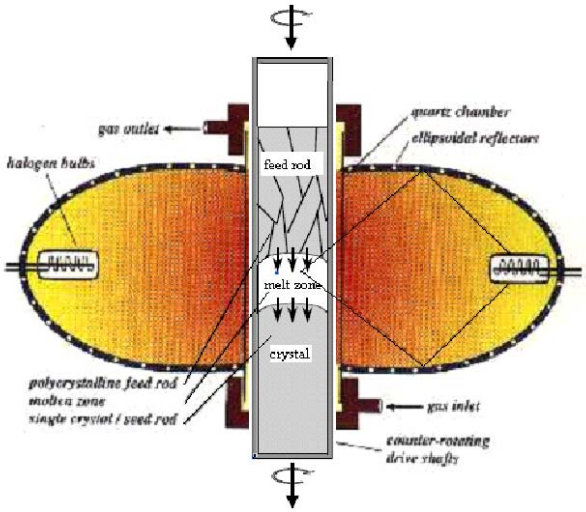
Densities of Te and liquid CZT:

Te: 5.7 g/cm^3
and
CZT (Zn=0.1): 5.5 g/cm^3

Density of Te droplets causes a higher concentration near the melt-solid interface, where they can become trapped in the growing crystal

Strategy and Technical Approach





Inverted Growth:

Dense Te droplets sink away from the melt-solid interface

Fills space in the seed pocket, so no room for Cd vapor and condensate

U-shape ensures contact of liquid to solid

Better Mixing of the Melt:

Rapid rotation using floating zone

Thin melt zone

Thermal Annealing:

Uniform temperature

Temperature gradient

Background on Crystal Growth

Various crystal growth methods have been used to grow CZT crystals in the last 50 years:

1. Traveling heater method[1],
2. Vertical gradient freezing[2],
3. High pressure Bridgman[3],
4. Electro-dynamic gradient techniques[4],
5. Horizontal Bridgman[5],
6. Vertical Bridgman[6],
7. Physical vapor transport[7], and
8. Czochralski method [8].

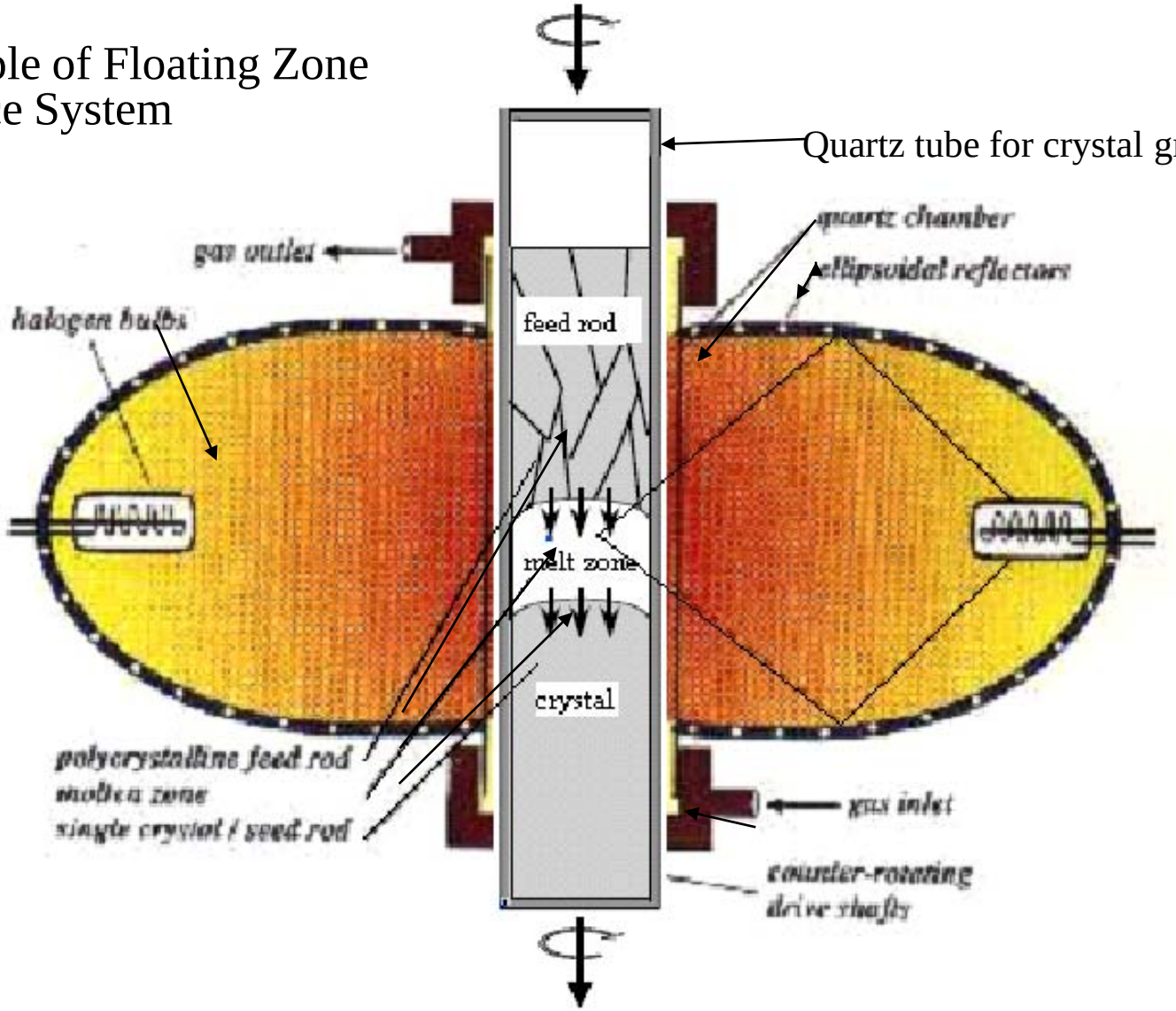
[1] R. Triboulet and G. Nen, **J. Cryst. Growth**, 65(1983)262.
[2] T. Asahi, O. Oda, et al, **J. Cryst. Growth**, 149(1995)23, 131(1996)20.
[3] F. P. Doty et al, **J. Vac. Sci. Tehnol. B**, 10(4)(1992)1418.
[4] C. Szeles et al, **IEEE Transations on Nuclear Sciene**, 49(2002)2535.
[5] K. Edwards et al, **J. Cryst. Growth**, 179(1997)133, 206(1999)37.
[6] Q. Li et al, **J. Cryst. Growth**, 233(2001)791.
[7] A Myielski et al, **J. Cryst. Growth**, 197(1999)423.
[8] H. M. Hobgood, **J. Cryst. Growth**, 85(1987)510

Get Bridgman growth equipment in place and operational

- Two 3”-diameter Bridgman growth furnaces
- Synthesis furnace
- CZT purification system
- Two annealing furnaces
- Graphite coating system
- Quartz cutting machine and sealing tool
- 3 new labs for growth and characterization
- 6” wire saw
- Lapping and polishing equipment
- New clean room space funded by BNL (under construction)

New Method: Floating Zone Furnace System

Principle of Floating Zone Furnace System



BNL has long history with floating zone method

Growth Furnace

Gold coated mirrors

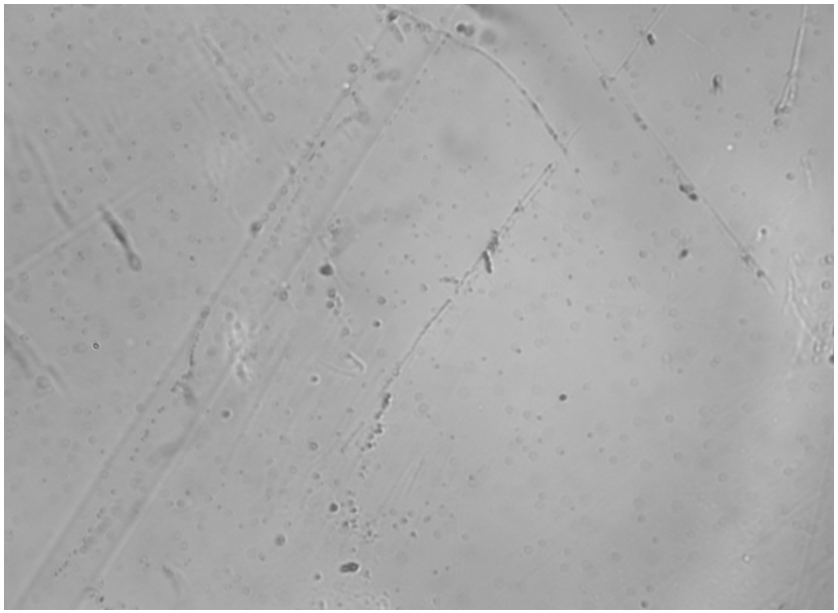
Multiple growth runs in Year 1

Example: Indium-doped $Cd_{0.9}Zn_{0.1}Te$ single crystal ingot with 2-cm diameter and 30-cm length

Single crystal growth demonstrated!

Inclusion-free-growth of CZT Crystals Demonstrated

$Cd_{0.9}Zn_{0.1}Te$ single crystals free of large Te inclusions were grown. Results consistent with inclusion formation – not precipitation!



(a)

(b)

Infrared transmission micrographs (Magnification at 500x)
(a) v = 2 mm/h, rotation at 6 rpm; (b) v = 0.1 mm/h, rotation at 60 rpm.

Can we produce high-resistivity CZT (> 10^9 ohm-cm)?

0.5-ppm indium doped

2-ppm indium doped

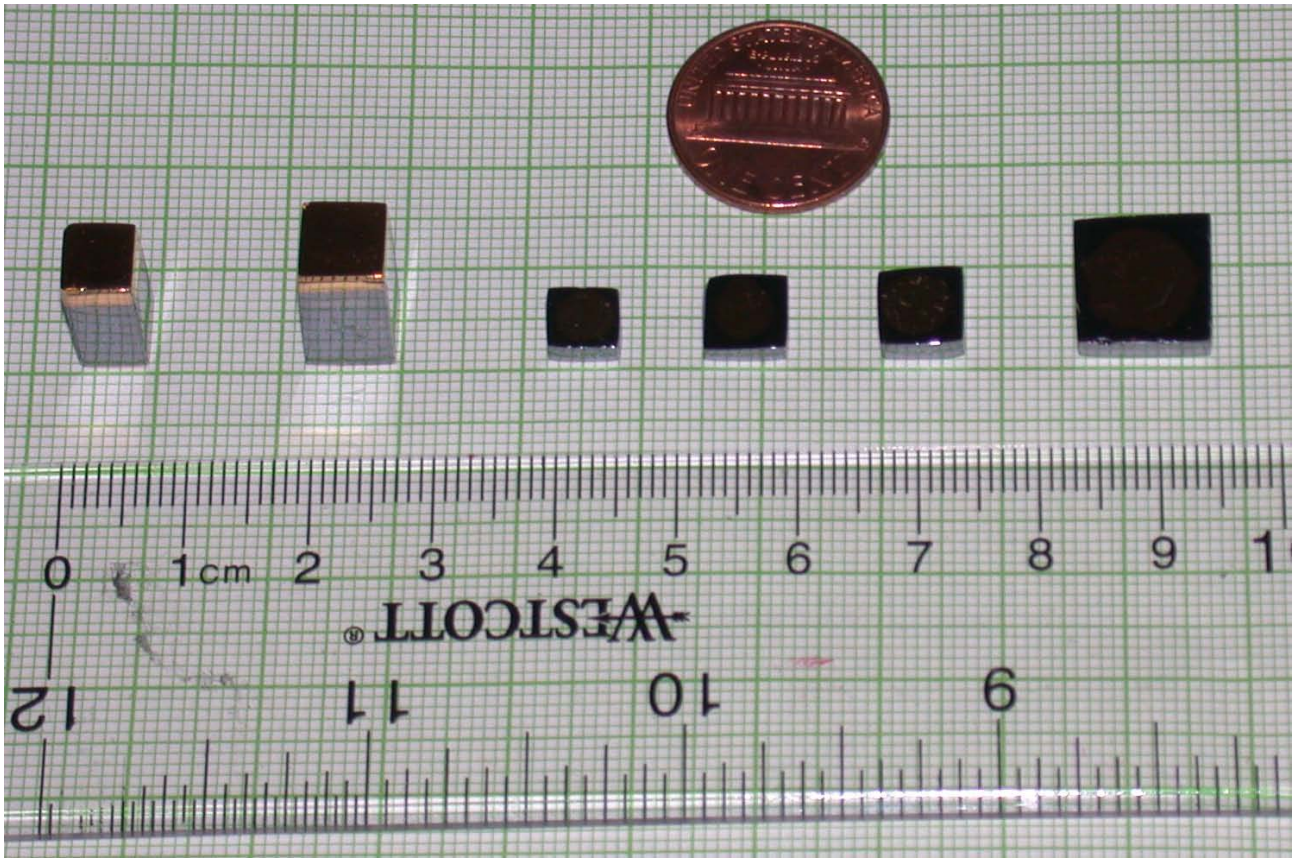
15-ppm indium doped

Results of Resistivity Experiments

- The resistivity of Cd-rich crystals is 10^2 ohm-cm and Te-rich undoped crystals are 10^6 ~10^7 ohm-cm.
- 0.1 ppm In doping is enough to increase the resistivity of the Te-rich crystals up to 10^{10} ohm-cm.
- The resistivity of Te-rich crystals with 15-20%Zn and indium doping is higher than 10^{11} ohm-cm.

Good News: High resistivity achieved! Key factors are Te-rich and indium doping.

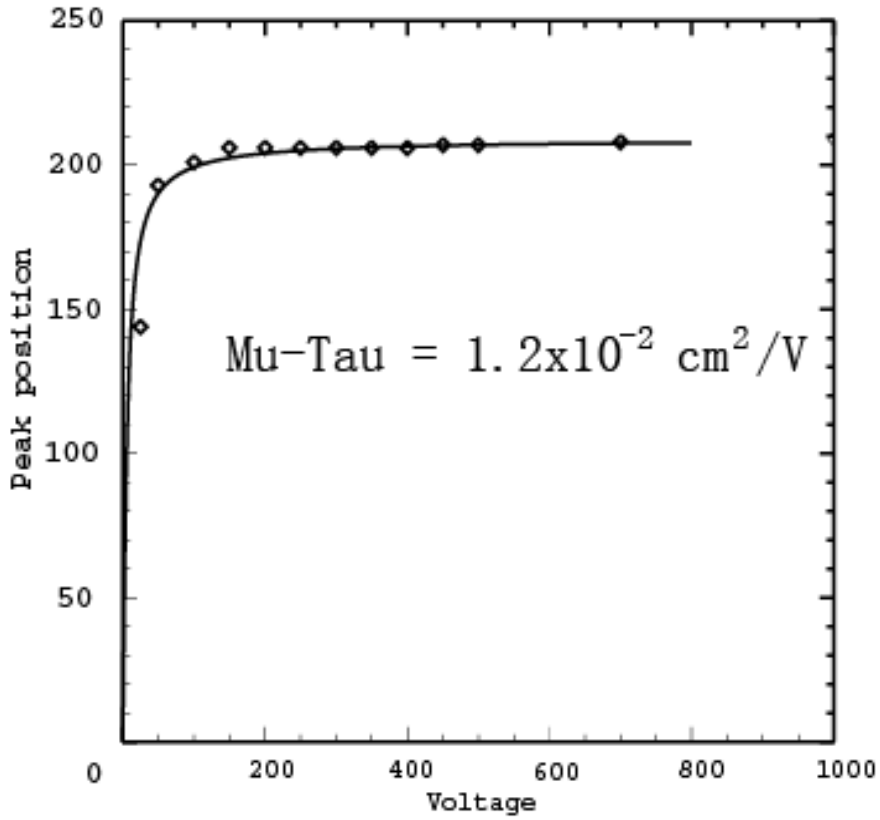
Detector Fabricated and Evaluated



15-ppm indium doped single-crystal $Cd_{0.9}Zn_{0.1}Te$

Excellent values for electron mobility-lifetime product observed

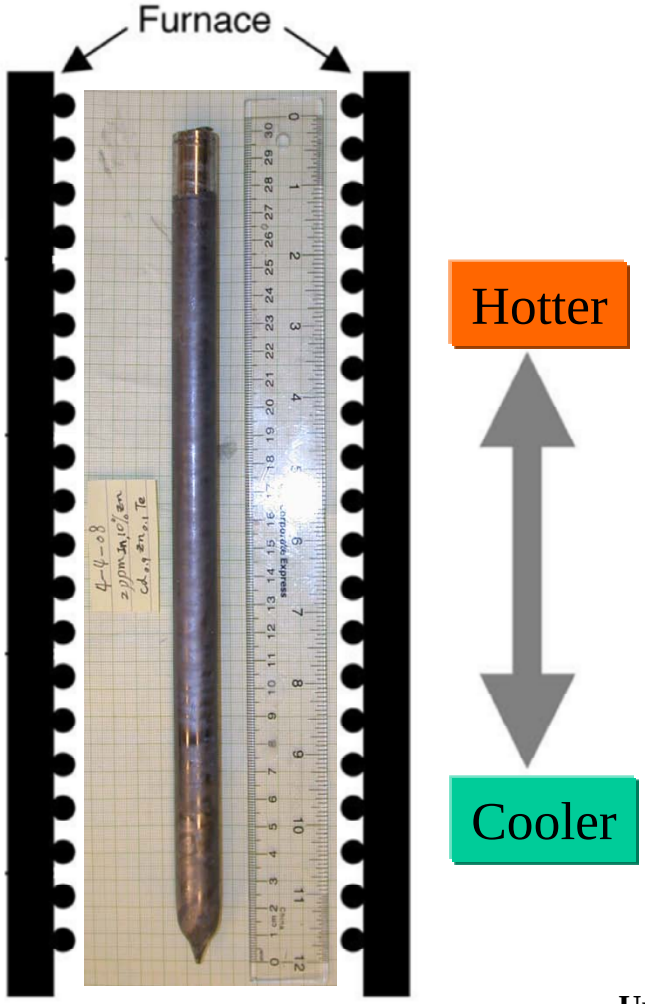
Typical values are in the mid 10^{-3} cm^2/V range

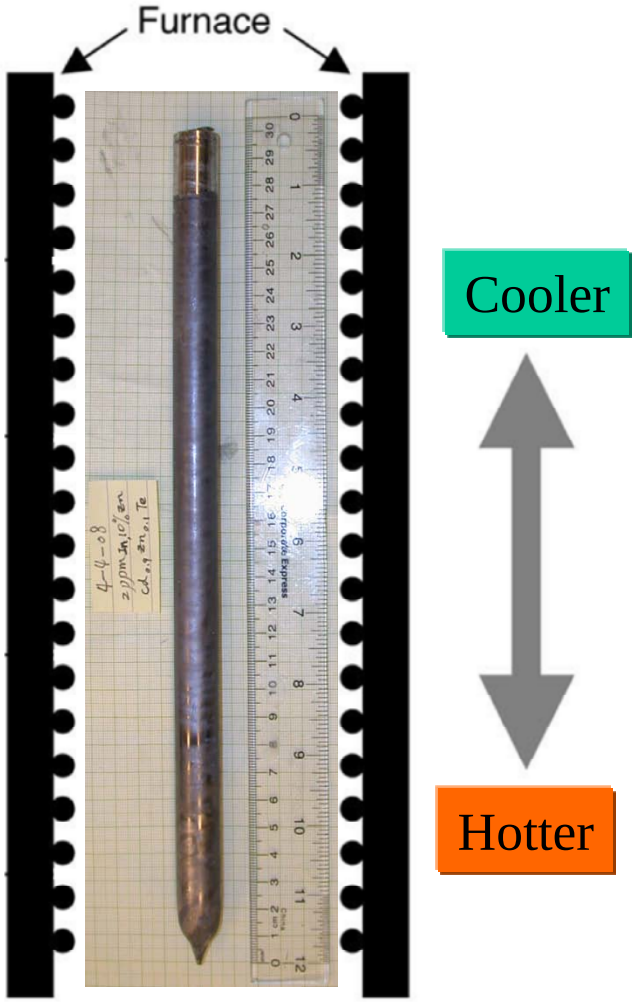


Planar detector of 10 x 10 x 3.7 mm^3. 6 μs shaping time.

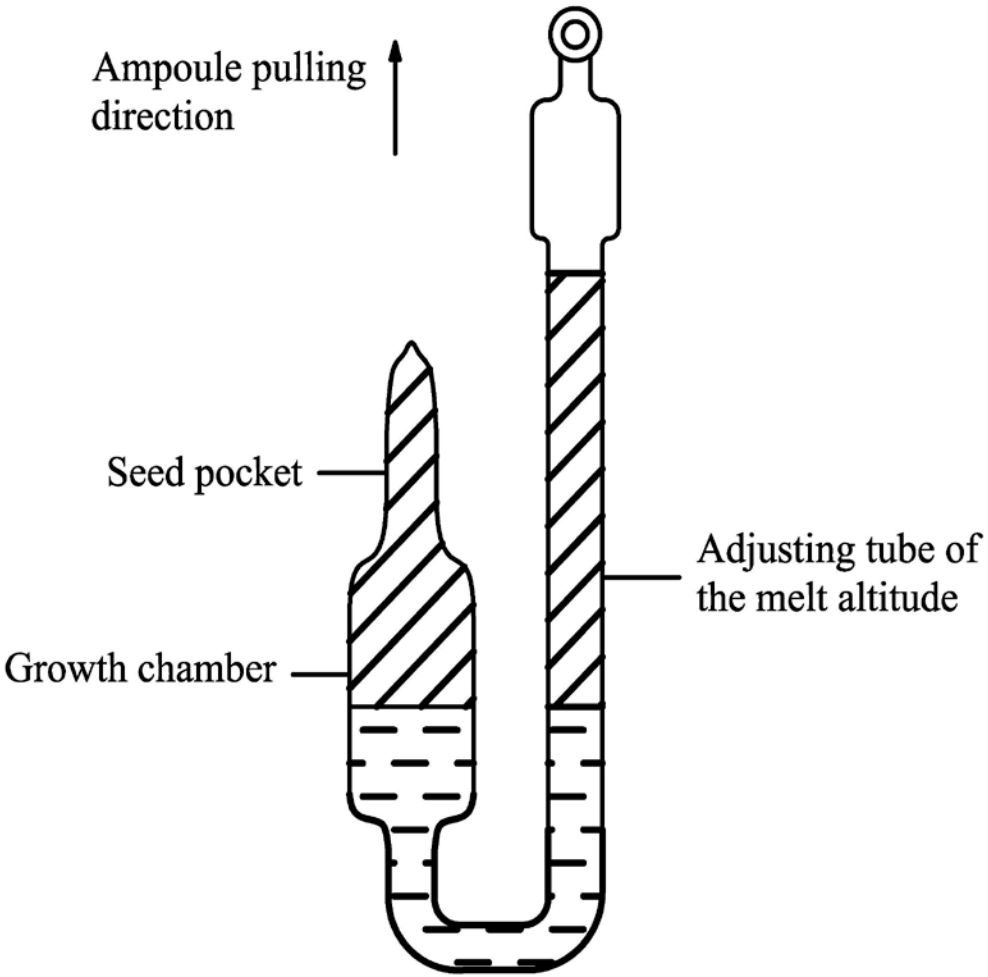
Inverted Growth with Floating Zone Method: Polycrystalline Material Produced

Reverse the temperature gradient to test inverted growth





Novel U-Shaped Ampoule Required to Ensure Melt-Solid Contact during Inverted Growth



Summary of Accomplishments and Future Work

- Demonstrated that floating zone method can be used to grow uniform CZT single crystals.
- Mixing of melt eliminated large Te secondary phases, supporting explanation based on inclusions. *New ways to solve the problem!*
- Indium doping in CZT crystals was a key factor to get high resistivity.
- Single crystals with high electron *mu-tau* 2-12 x 10^{-3} cm^2/V achieved by floating zone. *Rapid progress vastly exceeding expectations! New method for growth of detector-grade CZT demonstrated!*
- Inverted growth using the floating zone method did not work due to separation of the melt from the solid. *Consistent with initial thinking, but worth a try.*

Future Work:

- New Bridgman growth, synthesis and purification equipment delivered and installed. ESS&H requirements satisfied. *Ready for growth experimentation!*
- Complete inverted-growth experiments *with novel U-shaped ampoule design*

Thanks to NA22 for financial support!

Questions?