Office of Nonproliferation Research and Development

SNM Movement Detection / Radiation Sensors and Advanced Materials Portfolio Review

Correcting the Non-Uniformity in the Gamma-Ray Response of Large-Area CZT

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Research Team

Project started January 2006

Budget:  
FY06 - $400K  
FY07 - $540K  
FY08 - $565K + $125K*  
*Equipment budget

Budget Spent/Committed: $353,243
Budget Remaining: $212,757

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University sub-contractors: A. Burger, Fisk University and Y. C. Chang, University of Illinois.

Industrial collaborators: H. Chen, Redlen, Vancouver, BC, Canada; C. Szeles, eV Products, Saxonburg, PA; L. Li, Yinnel Tech, South Bend, IN; K. Mandel, EIC Labs, Boston, MA.

Other Universities: Fisk University (3), University of Michigan, Cornell University, Tennessee Technological University, Idaho State University, Chernivtsi National University, Vanderbilt University, and University of Freiburg.
Project Objectives and Long-Term Goal

1) Determine for the first time the properties limiting the performance of CZT detectors

2) Develop efficient, non-destructive techniques to measure the quality of detector materials

3) Provide rapid feedback to crystal growers and, in conjunction with suppliers, improve CZT detector performance as measured by device energy resolution, efficiency, stability and cost

Goal: Stable commercial supply of low-cost, high energy resolution (0.5% FWHM at 662 keV) CZT crystals for detecting, characterizing and imaging nuclear and radiological materials in a wide variety of field conditions
CZT is best candidate material today for room-temperature, solid-state nuclear radiation detectors. Broad applicability of CZT for nuclear nonproliferation applications is limited by three material problems.

(1) Poor hole collection

(2) Electron trapping by point defects

(3) Non-uniformity of single-crystal CZT

Known problems. Both electron and hole trapping can be corrected for uniform CZT detectors.

The importance of this problem was not recognized until large-volume single-crystal CZT became available. No effective electronic solution exists.
Approach: Understand and overcome the problem of non-uniformity in large-volume CZT detectors

BNL has developed unique tools to map the charge-collection uniformity in semiconductor detectors. Crystals are provided by Redlen, eV Products, Yinnel Tech, EIC, Orbotech, Eurorad, CIEMAT, IMEM-CNR, Institute of Solid-State Physics, and Univ. of Freiburg.

Example of a CZT wafer with multiple grain boundaries and twins.

Today single crystals up to 300 cm\(^3\) are available. But the device size is still limited to ~1-2 cm\(^3\). Attempts to use bigger crystals typically result in medium-to-low energy resolution.

For a long time this was a mystery – one that BNL was able to solve by using high-intensity X-ray beams at the National Synchrotron Light Source.

Journal of ELECTRONIC MATERIALS, Vol. 33, No. 6, 2004
Automated infrared mapping system assembled to quantify Te inclusions for different growth runs

- **Scans in the z (depth) direction with ~100um steps**
- **Algorithm applied that accurately records the size and number of the Te inclusions in different layers**
- **Good agreement with manual counting method**
Micro-scale detector mapping measurement

Using a MCA we record the energy spectrum for each point of the scanned detector area. Then we plot the peak channel vs. position.

10 μm x10 μm x-ray beam

10-μm tungsten collimator

Synchrotron radiation, 30-keV monoenergetic x-rays

CZT detector
Correlations between x-ray map & IR image

This x-ray map shows the degraded regions precisely correspond to Te inclusions on the right.

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

Very high correlation found for all CZT samples.
Response map near a Te inclusion

100 µm x 100 µm area
10-µm x 10-µm pinhole
5-µm step size
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!
Micro-scale variations in the electron mu-tau-product observed

Charge-collection efficiency map

$\mu\tau$ map

2x1.5 mm$^2$ area
1.5-mm thick
Spot size 10x10 $\mu$m$^2$
Measurements of concentration, distribution and size of Te inclusions

1. We count the # of Te inclusions (the algorithm rejects those out of focus) in each image
2. We calculate the concentration of Te inclusions in each volumetric region
3. We average over these 5 regions to calculate the concentration of Te inclusions per cm³

Results:

Concentration of Te inclusions per cm³
Distribution and sizes
Reconstructed region: 1x1x5 mm$^3$

Te inclusions represented by dark discs. Discs diameters equal to 5x (a) and 25x (b) of actual diameters of inclusions.

Inclusions often concentrate along the lines.

Typical concentration is $10^4 - 10^6$ cm$^{-3}$.

Typical excess of Te is 0.01 – 0.03 atomic %.

Total geometrical area is about 0.07 cm$^2$ per cm-thickness.
Reconstructed 3D distributions of Te secondary phases for different samples

CZT volume: 1x1.5x5 mm$^3$
Distributions of Te inclusions quantified

Te inclusions represented by dark discs (5x of actual diameters)

Size distribution of Te inclusions

Concentration: 3.8x10^5 cm⁻³
Te excess: 0.0092 at%
Measured vs. simulated X-ray maps

1-mm thick CZT sample
Energy 30 keV; beam size 10x10 um²
Inclusions size 1-20 um
Total concentration ~10⁵ cm⁻³

This comparison suggests that the effective and actual sizes of Te inclusions are close.
Simulations predict that Te inclusions with sizes of < 2 \( \mu \text{m} \) can be tolerated. They behave as ordinary traps. These results were confirmed from actual measurements!

FWHM (% @ 662 keV) of photo-peak vs. size (1-20 \( \mu \text{m} \) diameter) and concentration (up to \( 5 \times 10^6 \text{ cm}^{-3} \)) of Te inclusions.

The plots are calculated for a 1x1x15 mm\(^3\) voxel of an ideal single-carrier device irradiated with a \(^{137}\text{Cs}\) source.

Electric field is 2000 V/cm.

Simulations predict that Te inclusions with sizes of < 2 \( \mu \text{m} \) can be tolerated. They behave as ordinary traps.

These results were confirmed from actual measurements!
First high-resolution maps of hole mu-tau product

Hole charge-collection map

31keV; -170V
Spot size: 25um;
Conventional electron trapping (no Te inclusions) in a 15-mm thick device

Pulse-height spectrum simulated for a 1x1x15 mm$^3$ voxel of the ideal single-carrier detector.

The $\mu\tau$-product is $10^{-2}$ cm$^2$/V.

Electron trapping can be easily corrected!
Hypothesis: *Te secondary phases are caused by Te inclusions*

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.
Results point to new directions/thrusts for CZT growth and post-growth processing

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 presence of Te-rich inclusions

- Better mixing of the melt by rotation, magnetic stirring, or other means
- Modify ampoule design
- 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 closed systems or gas over-pressures
- Post-growth thermal annealing in Cd (or Zn) vapors
- In-situ time-resolved measurements of conductivity and Te-inclusion size and distribution under controlled heating and cooling rates
Large reductions in the size of Te inclusions possible

Detector A – Traveling Heater Method

Detector B – Bridgman Method

(FOV = 3.9mmx5.3mm, same magnification)
High-resolution X-ray response maps for different growth techniques

Mapping of CZT materials from two growth processes

THM

Bridgman
Floating zone method also works!

Using a floating zone method, we produced CZT with no inclusions with sizes $> 2 \, \mu \text{m}$, good mu-tau product, $3 \times 10^{-3}$ cm$^2$/V, and resistivity $> 10^{10}$ Ohm-cm. Full compensation at 0.1 ppm indium dopant.

Ingot dimensions: 20-mm diameter and 300-mm length

IR transmission
Post-growth thermal annealing also holds promise

Annealing in a gradient temperature found to reduce the Te inclusions and precipitates.

The sample after 4-day annealing in Cd vapour and in a temperature gradient of 10 K/cm
Conclusions

- Project results have simulated many new ideas on characterization of Te inclusions/precipitates, different growth methods, and post-growth annealing experiments.
- Use of CZT detectors is limited by the availability of uniform, large-volume CZT crystals.
- The first-order problem is the presence of grain boundaries and twins. Much progress has occurred.
- The primary problem for single-crystal CZT is Te inclusions causing large fluctuations in the electron trapping.
- With improvements in material uniformity, CZT can potentially replace traditional materials used for detection of gamma radiation in many nonproliferation applications.

- Without improvements in the CZT crystal growth process, a stable supply of large-volume spectrometers is unlikely.
Future Directions

• Use unique mapping tools to help national labs, industry, and academic researchers

• What is the nature and origin of the secondary phases (inclusions vs. precipitates)?

• How can we eliminate the large inclusions during growth (rotation, magnetic stirring, inverted growth, etc.)?

• What is the most effective post-growth thermal annealing process?

• Do inclusions getter impurities?

• What are the residual defects after annealing?

• What is the role of charging of inclusions and surfaces on the internal E field and charge-collection efficiency?
33 Peer-Reviewed Publications


33 Peer-Reviewed Publications (continued)


33 Peer-Reviewed Publications (continued)


33 Peer-Reviewed Publications (continued)


35 Presentations, 2 IEEE National Awards and 1 Patent

- “Advanced Nuclear Detectors to Interdict Smuggling Events”, NATO Workshop on Countering Nuclear and Radiological Terrorism, Yerevan, Armenia, October 3-7, 2005.
- “CdTe and Cd$_{0.9}$Zn$_{0.1}$Te Crystal Growth and Characterization for Nuclear Spectrometers”, SPIE Conference on Hard X-Ray and Gamma-Ray Detector Physics VIII, San Diego, CA, August 15, 2006.
35 Presentations, 2 IEEE National Awards and 1 Patent


- “Characterization of Low Defect Cd_{0.9}Zn_{0.1}Te and CdTe Crystals for High Performance Frisch Collar Detectors”, 15th International Room-Temperature Semiconductor Detector Workshop, San Diego, CA, October 30, 2006.


- “Te Precipitates in CdZnTe (Zn=10%) Radiation-Detection Materials”, 15th International Room-Temperature Semiconductor Detector Workshop, San Diego, CA, November 1, 2006.

35 Presentations, 2 IEEE National Awards and 1 Patent


- “Room-Temperature Semiconductor Radiation Detectors”, University of Connecticut, October 12, 2007, Storrs, CT.

- “Studies of the Effects of Te Inclusions in CdZnTe Radiation Detectors”, IEEE Nuclear Science Symposium, October 31, 2007, Honolulu, HA.
35 Presentations, 2 IEEE National Awards and 1 Patent


• “CZT Gamma-Ray Detectors”, University of Michigan Colloquium, April 4, 2008, Ann Arbor, MI.

• “Room-Temperature Semiconductor Gamma Detectors”, University of Freiburg Seminar, April 14, 2008, Freiburg, Germany.

• “The Effect of Te Inclusions in Cadmium Zinc Telluride Radiation Detectors”, NA22 Workshop on CZT Detectors, April 23, 2008, Washington State University, Pullman, WA.


National Awards:

(1) 2006 IEEE Radiation Instrumentation Outstanding Achievement Award

(2) 2007 IEEE Harold Wheeler Award

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Thank You!
Energy resolutions of <0.8% achievable for long-drift detectors

Responses of two detectors fabricated from different growth runs

- High concentration of 3-20-micron inclusions, \( \sim 10^5 \text{ cm}^{-3} \).
- High concentration of 1-2-micron inclusions, \( \sim 10^6 \text{ cm}^{-3} \).

Energy resolution of 3.8% at 662 keV
6x6x12 mm\(^3\)

Energy resolution of 0.75% at 662 keV
4.5x4.5x11 mm\(^3\)
Correlation between electron and hole collection maps observed

1.5-mm thick CZT sample

Electron Map

20 keV X rays; Cathode bias 280 V; Resolution 10 mm; 91x41 pixels

Hole Map