BNL-113706-2017-CP

**CdxZn1-xTeySe1-y (CZTS):
An Emerging High-Performance Gamma-Ray Detector**

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*Presented at the Nuclear Security Applications and Development Program Review Meeting (NSARD2017)
Brookhaven National Laboratory, Upton, NY
NNSA North Las Vegas Facility, Las Vegas, NV
April 4-6, 2017*

April 2017

Nonproliferation and National Security Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE National Nuclear Security Administration (NNSA),
Office of Defense Nuclear Nonproliferation (NA-20)**

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Defense Nuclear Nonproliferation Research & Development

Nuclear Security Applications Research & Development Portfolio Review *NSARD 2017*

$\text{Cd}_x\text{Zn}_{1-x}\text{Te}_y\text{Se}_{1-y}$ (CZTS): An Emerging High- Performance Gamma-Ray Detector

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April 5th, 2017

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Project overview

- ❑ Today, cadmium zinc telluride (CZT) is the most advanced room-temperature semiconductor material for gamma-ray detection.
- ❑ However, CZT suffers from 3 major detrimental defects
 - Non-unity segregation of Zn
 - Crystal defect (sub-grain boundary) network
 - High concentrations of Te inclusions/precipitates

(a) THM-grown CZT ingot cut along the length, (b) Zn concentration mapping and (c) Zn concentration along the length of the ingot.

Roy et al. *J. Crystal Growth* 347 (2012) 53.

X-Ray diffraction topography images showing $\sim 1 \text{ cm}^2$ areas of detector-grade CZT samples supplied by seven different vendors.

A. E. Bolotnikov et al. *J. Cryst. Growth* 379 (2013) 46.

- These issues cause low yield and high cost of CZT radiation detectors, limiting their applications.
- Researchers have tried to solve the issues by improving the crystal growth process and post-growth annealing, but have not mitigated all disadvantages.

Project goal and deliverables

The goal of the proposed project is to develop **as-grown** CZTS radiation detectors with high compositional uniformity, better performance, higher yield and lower cost than today's CZT.

Deliverables:

- ☐ Growth of eight CZTS ingots per year.
- ☐ Characterization of the as-grown ingots:
 - X-ray topography, IR microscopy, compositional uniformity by EDS and X-ray fluorescence, photoluminescence (PL), DLTS, I-V, and charge-transport characterization.
- ☐ Detector fabrication and test.
- ☐ Compute maps of band gap and band edge positions for CZTS alloy across the composition range of Zn and Se.
- ☐ Compute thermodynamic stability and phase separation of CZTS alloy as a function of composition and temperature.
- ☐ Compute accurate prediction of defect levels across alloy compositions

Growth and characterization

- ❑ CZTS ingots were grown by traveling heater method (THM) as well as vertical Bridgman Method (BM).
 - 6N purity CdZnTe and CdSe were used for synthesis of the CZTS compound.
 - 6N purity Te was used as solvent for THM growth.
- ❑ Although BM technique is being used for crystal growth, our main thrust is THM growth of CZTS for its following advantages:
 - Low-temperature growth
 - Less chance of incorporation of impurities from the crucible during growth
 - Less/no chance of ampoule explosion
 - Enhanced purity of the ingot
 - Fewer defects due to the lower growth temperature
- ❑ Crystals were cut and polished for various characterizations and detector fabrication and testing.

CZTS ingots

- ❑ We are focusing on THM-growth of 2-in diameter CZTS ingots with different elemental compositions:

$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ ingots:

40-mm diameter ingot grown by BM (undoped).

In-doped 52-mm diameter ingot grown by THM (fast cooled ingot).

$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.96}\text{Se}_{0.04}$ ingots:

40-mm diameter ingot grown by BM (undoped).

In-doped 52-mm diameter ingot grown by THM.

$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ ingots:

40-mm diameter ingot grown by BM (undoped).

In-doped 52-mm diameter ingot grown by THM.

Unclassified

Optimization of growth parameters (THM)

THM growth is highly sensitive to growth parameters.

- i. Width of Te-rich solution zone
- ii. Growth temperature
- iii. Temperature gradient near the growth interface

Schematic of growth interface shape
A) convex, B) concave and C) flat.

Convex and flat growth interfaces are favorable for growth of large grain and single crystalline ingots.

Flat interfaces are desired for seeded growth.

Growth interface (THM)

Concave interface of 52-mm diameter $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ ingot grown by THM.
The very first CZTS ingot.

Slightly convex nearly flat interface of 52-mm diameter $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ ingot grown by THM.

Slightly convex nearly flat interface of 52-mm diameter $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.96}\text{Se}_{0.04}$ ingot grown by THM.

Since our goal is seeded growth, we are focusing on achieving slightly convex and nearly flat growth interface.

Compositional distributions in CZTS

Composition of Zn and Se is fairly uniform throughout the ingot for $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$. Especially the calculated band gap.

For 2% and 4% Se composition, the band gap of the ingots is fairly uniform within the experimental accuracy. It only decreases in a narrow region (< 1 cm) near the interface.

~90% of the ingot shows uniform band gap for both 2 and 4% Se composition).

On the contrary, for THM grown CZT, only about one third of the ingot shows uniform composition.

Zn and Se composition and the calculated band gap along the length of the THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$, $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ and $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.96}\text{Se}_{0.04}$ ingots: from top to bottom.

X-ray topographic analyses

Optical photograph of lapped, and X-ray topographic pictures of Bridgman grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ sample of dimensions $5 \times 6 \times 11 \text{ mm}^3$

a)- c): X-ray topographic pictures of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ sample and the corresponding optical photography of the grains.

a) X-ray topographic, b) photograph of the polished sample in reflection mode and c) IR transmission picture of a THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ sample. Dimensions: $8 \times 5.6 \times 2.5 \text{ mm}^3$ and $8.2 \times 7 \times 1.55 \text{ mm}^3$.

X-ray topographic picture and photograph of the polished sample. The surface area is $\sim 15 \times 10 \text{ mm}^2$.

Higher Se concentration is more effective in arresting sub-grain boundary. No sub-grain boundary network was evidenced.

Sub-grain boundary network problem is alleviated for CZTS material.

Concentrations and size distribution of Te inclusions in CZTS

For both Bridgman and THM grown $Cd_{0.9}Zn_{0.1}Te_{0.93}Se_{0.07}$ ingots, concentrations of Te inclusions/precipitates were found **8-9 times** lower than in standard CZT.

Evaluation of size distribution of Te inclusions/precipitates for $Cd_{0.9}Zn_{0.1}Te_{0.98}Se_{0.02}$ and $Cd_{0.9}Zn_{0.1}Te_{0.96}Se_{0.04}$ ingots will be performed soon.

Low-temperature Photoluminescence of CZTS

PL-spectrum: BM-grown un-doped and THM-grown In-doped $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ at 4.2 K.

A-centers seem to be reduced with increased Se concentrations.

PL-spectrum: THM-grown In-doped $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ at 7 K.

Roles of Se

- **Strong influence in modifying Zn segregation coefficient: better compositional homogeneity with increased Se concentration.**
- **Effective solution hardening in arresting sub-grain boundaries and their network with increased Se content.**
- **Decreased Te-inclusion/precipitate concentration with increased Se content.**
- **Decrease of A-center with increased Se content.**

Unclassified

Resistivity mapping of CZTS 2-inch wafer

(a) IR transmission image; and (b) resistivity map at room temperature of 4.2-mm thick $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ wafer grown by THM.

(a) IR transmission image; and (b) resistivity map at room temperature of 3.3-mm thick $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ wafer grown by THM.

PL map of CZTS 2-inch wafer

Room temperature photoluminescence (PL) map of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ two inch wafer grown by THM. The map area is $4 \times 4 \text{ cm}^2$. Step size 2 mm.

Variation of the peak energy (peak 1) over the entire scan area, ΔE is ~ 2 meV, thus the composition and band gap are highly uniform over the $4 \times 4 \text{ cm}^2$ area.

Composition and band gaps are highly uniform for both 2% and 7% Se containing CZTS wafers.

Low temperature (7K) photoluminescence (PL) map of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ two inch wafer grown by THM. The map area is $\sim 2.8 \times 3 \text{ cm}^2$. Step size 1 mm.

Variation of the peak energy (A^0,X and D^0,X) over the entire scan area, ΔE is ~ 1.5 meV, thus the composition and band gap are highly uniform over the $2.8 \times 3 \text{ cm}^2$ area.

Theory guiding optimization of resistivity: band edge bowing

- **Computed absolute band edge energies across composition range helps choose best compositions**
 - Band edges contribute to intrinsic resistivity, dopant compensation and impurity trap levels (also next slide)
 - Band edge engineering can also help design optimal contacts

Theory guiding optimization of resistivity: Point defects

Dangling bond analysis

Point defect properties of
end-point binaries

Descriptors for interpolation
using machine learning

- Various computational machinery developed for accurate prediction of defect levels across alloy compositions
 - Dangling bonds, band edge positions, machine learning
 - Allows optimization of dopants with composition and comparison to DLTS experiments for validation
 - Applied to cation vacancies, other defects/impurities on-going

Charge transport properties of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$

Charge collection versus applied bias voltage

- ^{241}Am source
- Planar detector: $6.65 \times 5.75 \times 1.86 \text{ mm}^3$

- ^{241}Am source
- Planar detector: $5.65 \times 5.18 \times 2.8 \text{ mm}^3$
- Sample with more Te-inclusions/precipitations

In general the $\mu\tau$ product varies between $4.5\text{-}6 \times 10^{-3} \text{ cm}^2/\text{V}$.

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Detector response of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$

- (a) Picture of the detector: $4.4 \times 4.4 \times 10 \text{ mm}^3$
 (b) Reflection mode microscopic scan
 (c) IR transmission image

I-V characteristics at room temperature. Inset: I-V for 0-1V.

Bias voltage: 1800V
Shaping time 3 micro sec.

Device response of the very first virtual Frisch grid detector

Bias voltage: 2300V, (Frisch grid~7mm long)
Shaping time 10 μs .

Bias voltage: 2300V, Shaping time 6 μs .

All the spectra are as-measured without any correction technique.

Unclassified

Detector response of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$

Device response of the very first virtual Frisch grid detector (cont'd)

**HV: -2300V,
Shaping time 10 μs**

All the spectra are as-measured without any correction technique.

Electric field estimation of THM-grown

$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ VFG detector

a

b

c

IR transmission image of the detector

a) Under parallel polarizer

b) Cross polarizer with 0 V

c) Cross polarizer with 2500 V.

The detector dimensions: $4.4 \times 4.4 \times 10 \text{ mm}^3$.

No residual stress was observed under the cross polarizer for all four VFG detectors fabricated.

Unclassified

Best CZTS virtual Frisch-grid detector

Device response of the best virtual Frisch grid detector.

Resistivity: 2.6×10^{10} ohm-cm

Left: Picture of the detector: $3.6 \times 3.4 \times 9.7$ mm³

Right: microscopic scan IR transmission image

Bias voltage: 1800V, Shaping time 6 micro sec (Frisch grid~3mm long)

All the spectra are as-measured without any correction technique.

Best CZTS virtual Frisch-grid detector

Device response of the best virtual Frisch grid detector.

Bias voltage: 1800V, Shaping time 3 micro sec

*Bias voltage: 1800 V
Shaping time 6 μs*

Bias voltage: 1800 V, Shaping time 6 μs

All the spectra are as-measured without any correction technique.

Detector response of THM-grown

 $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ at different shaping time **a** **b** **c** **d**

Response of VFG detector at different shaping time a) 2 μ sec, b) 3 μ sec, c) 6 μ sec and d) 10 μ sec.
The detector dimensions: 4.8x4.9x9.7 mm³. (Frisch grid~4mm long)

Detector response of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ under different bias voltage

The detector dimensions: $3.4 \times 3.4 \times 9.15 \text{ mm}^3$. (Frisch grid~3mm long)

In spite of moderate μr value, the device is operating even at low voltages.

Detector quality at a glance

IR image

Dimensions: $4.4 \times 4.4 \times 10 \text{ mm}^3$
 I at 500V : 1.77 nA
 Resistivity : $1.2 \times 10^{10} \text{ ohm-cm}$
 Resolution
 at 662 keV : ~ 2%
 FG length : 7mm

IR image

Dimensions: $3.4 \times 3.4 \times 9.15 \text{ mm}^3$
 I at 500V : 0.57 nA
 Resistivity : $1.5 \times 10^{10} \text{ ohm-cm}$
 Resolution
 at 662 keV : ~ 1.6%
 FG length : 3mm

Detector qualities are comparable to good quality CZT available today.

Quasi-hemispherical detector response:

IR image

Dimensions: $3.4 \times 3.6 \times 9.7 \text{ mm}^3$
 I at 500V : 0.77 nA
 Resistivity : $2.6 \times 10^{10} \text{ ohm-cm}$
 Resolution
 at 662 keV : ~ 1.3%
 FG length : 3mm

IR image

Dimensions: $4.8 \times 4.9 \times 9.7 \text{ mm}^3$
 I at 500V : 1.26 nA
 Resistivity : $3 \times 10^{10} \text{ ohm-cm}$
 Resolution
 at 662 keV : ~ 1.9%
 FG length : 4mm

Dimensions: $7.34 \times 6.35 \times 4.5 \text{ mm}^3$
 E-res. at 662 keV: ~ 3%

Dimensions: $10.6 \times 10.3 \times 10 \text{ mm}^3$
 E-res. at 662 keV: ~ 4.5%

All the charge transport characteristics and the detector responses are performed on as-grown THM CZTS ingots.

Unclassified

Technical challenges and future work

Technical Challenges

- Increase grain size of the ingots.
- Make special efforts to increase the resistivity up to 2×10^{10} ohm-cm for THM grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ ingots.

Future Work

- We have optimized the growth parameters for seeded growth to get slightly convex interface. Seeded growth will be carried out for two inch THM growth.
- Characterization of the as-grown ingots will continue serving as feedback towards improving the material growth process.
- Fabrication of detectors larger than 1 cm^3 with enhanced charge transport properties.

Acknowledgments

We thank the Office of Defense Nuclear Nonproliferation Research & Development (DNN R&D) for supporting this work.

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Quaternary material produces better crystals with less strain and very high compositional uniformity

Background/State of the Art

- Today, CZT is the most advanced room-temperature semiconductor material for gamma-ray detection.
- However, it suffers from 3 major detrimental defects (non-unity segregation of Zn, sub-grain boundary dislocation networks, and Te inclusions).
- These issues cause low yield and high cost of CZT radiation detectors, limiting their applications.
- Researchers have tried to solve the issues by improving the crystal growth process and post-growth annealing, with limited success.

Innovation

- Selenium in the CZT matrix was found to be effective in arresting sub-grain boundary networks and producing compositional homogeneity and lower concentration of Te inclusions.
- All these defects have deleterious effects on μr . Since we have drastically reduced these defects in CZTS, we believe that the μr values can be improved significantly compared to CZT.
- Thus CZTS has tremendous potential for the production of high-performance detectors at a substantially lower production cost.

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Approach, Metrics and Outcomes

MAIN ACHIEVEMENT

- The goal is to develop growth technology to produce CZTS radiation detectors better than today's large-volume CZT and at a lower price.

HOW IT WORKS

- By introducing Se in CZT material, we are able to use the Traveling Heater growth method (THM) to produce high-quality CZTS crystals with uniform composition and reduced dislocation networks using THM growth. Comparison to Bridgman grown crystals is also being pursued.
- We are using modified THM growth at a lower temperature gradient compared to the conventional technique to produce detector-grade CZTS without requiring post-growth wafer annealing, which is needed for CZT.
- We are using first-principles theory to guide choice of ingot compositions for optimum bandgap and to characterize remaining deleterious defects to help improve resistivity.
- We achieved very high μr values within a very short period of research, as compared to CZT development.

ASSUMPTIONS AND LIMITATIONS

- The current results obtained in the short period of ~ 5.5 quarter (high μr , 1.3% resolution (as measured) for virtual Frisch grid detector at 662 keV) are very promising. We are optimistic to achieve the end goal upon completion of the project.
- The results achieved so far are highly encouraging and the detector performance is equivalent to high quality CZT presently available, indicate very low risk level and potentially high pay-off.

Impact

- This project will result in a technology for producing a better room-temperature semiconductor detector at lower cost.
- The technology will allow gamma-ray detection with high energy resolution and high detection efficiency per unit volume.
- The technology is needed by federal agencies (DOE, DOD and DHS) and the IAEA for nuclear and radioactive material detection and imaging.
- Manufacturers of medical imaging devices will also be interested in this novel material to enhance the performance of their imaging devices and reduce the material cost.

TRLs: start at TRL2 and finish at TRL3

Goals/Action Plan

Current FY

- Produce 8 CZTS ingots & fabricate high quality detectors.
- Compute electronic properties of native point defects across CZTS composition range.

Future FY

- Seeded growth of CZTS by THM
- Compute electronic properties of impurities and defect complexes in CZTS alloy to guide further improvements in resistivity and validate against experiments

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