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

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Nonproliferation and National Security Department
Brookhaven National Laboratory

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Defense Nuclear Nonproliferation Research & Development

Nuclear Security Applications Research & Development Portfolio Review

NSARD 2018

$Cd_xZn_{1-x}Te_ySe_{1-y}$ (CZTS): An Emerging High-Performance Gamma-Ray Detector

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April 17th, 2017

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Project goal and deliverables

The goal of the proposed project is to develop CZTS radiation detectors with

High compositional uniformity.
Fewer defects.
Better performance.
Higher yield and lower cost than today's CZT.

All from as-grown ingots !!!

Deliverables:

- **Growth of two inch diameter CZTS ingots.**
- **Characterization of the as-grown ingots:**
  - **X-ray topography, IR microscopy, compositional uniformity by EDS and X-ray fluorescence, photoluminescence (PL), I-V, and charge-transport characterization.**
- **Detector fabrication and test.**
- **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**

So far, how is it done today and the limits?

High compositional uniformity:

About 90% of the ingot length showed uniform composition. Photoluminescence peak position (reflects the band gap) was found to vary (ΔE) within ~2-1.5 *meV* over ~16 and 9 cm^2 area of the wafer cut perpendicular to ingot axis.

Fewer defects:

For 7% Se composition, no sub-grain boundary was observed. For 2% Se, very few sub-grain boundaries were observed and no network was observed.
Concentration of Te-inclusions was found to be much lower compared to CZT.

Better performance:

All the Frisch-grid detectors fabricated from 2% Se CZTS ingot, showed energy resolution less than 2% at 662 keV.

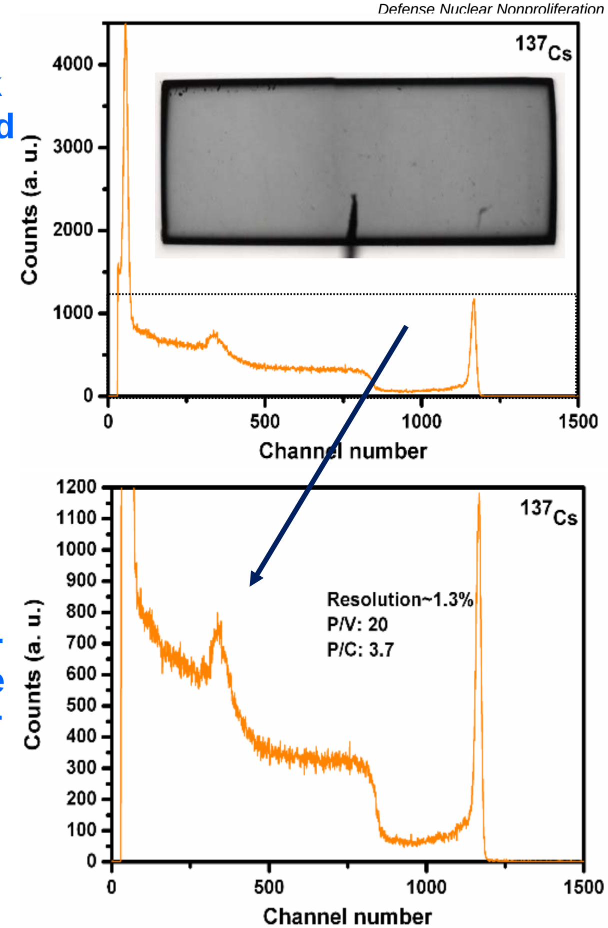
Higher yield and lower cost than today's CZT:

Higher compositional uniformity (~90%) results in overall higher yield.
Fewer defects, absence of sub-grain boundary network and lower concentration of Te-inclusions can result in higher yield of high quality detectors. Detectors can readily be fabricated from as-grown ingots. So, the overall cost is expected to be 3-4 times lower for high quality detectors compared to CZT.

At present, we have optimized the composition with 2% Se and 10% Zn for best $\mu\tau$ (6.6×10^{-3} cm^2/V) and detector response, among the compositions of 4% and 7% Se.

Limits of the current practice:

Smaller grain size, and # of furnaces.



Typical Frisch-grid detector response from as-grown CZTS with 2% Se. Applied bias: 1800 V. Detector dimensions: 3.6x3.4x9.7 mm^3

What is new in our approach

Role of Se in CdZnTe matrix

- **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.**

With the addition of selenium, the overall cost of the CZTS detectors is expected to be 3-4 times lower especially for high quality detectors compared to CZT, without compromising detector response.

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Who cares?

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- This project will result in a technology for producing better room-temperature semiconductor detectors at lower cost for non-proliferation missions.
- The technology will allow gamma-ray detection with high energy resolution and high detection efficiency per unit volume at much lower cost of production.
- The technology is needed by federal agencies (DOE, DOD and DHS) and the IAEA for nuclear and radioactive material detection, isotope identification 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.

Unclassified

Risks and technical challenges

Risk

Risks include difficulties (a) to grow large diameter ingots (b) to achieve high resistivity and (c) to achieve high mobility-lifetime product.

Looking at the progress on the CZTS project, we believe that the risk factor is very much less than originally anticipated.

Technical Challenges

- **Increase grain size of the ingots. Can be resolved by seeded growth.**
- **Purity of the starting material especially CdSe.** ***Concentrations of deep level impurities present in the raw CdSe is high.*** **We have procured 7N purity Cd and 6N purity Se and will synthesize and purify CdSe in house.**
- **Make special efforts to increase the resistivity up to $2x10^{10}$ ohm-cm for THM grown $Cd_{0.9}Zn_{0.1}Te_{0.93}Se_{0.07}$ ingots.**
- ***Increased number of furnaces will lead to faster R&D output.***

Recent progress (to date)

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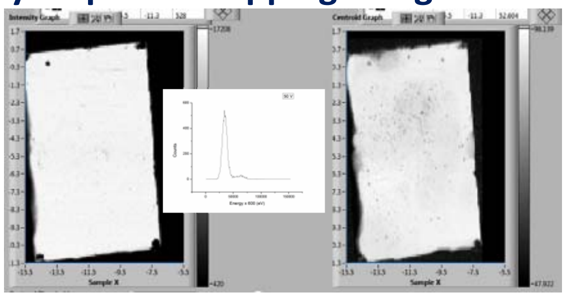
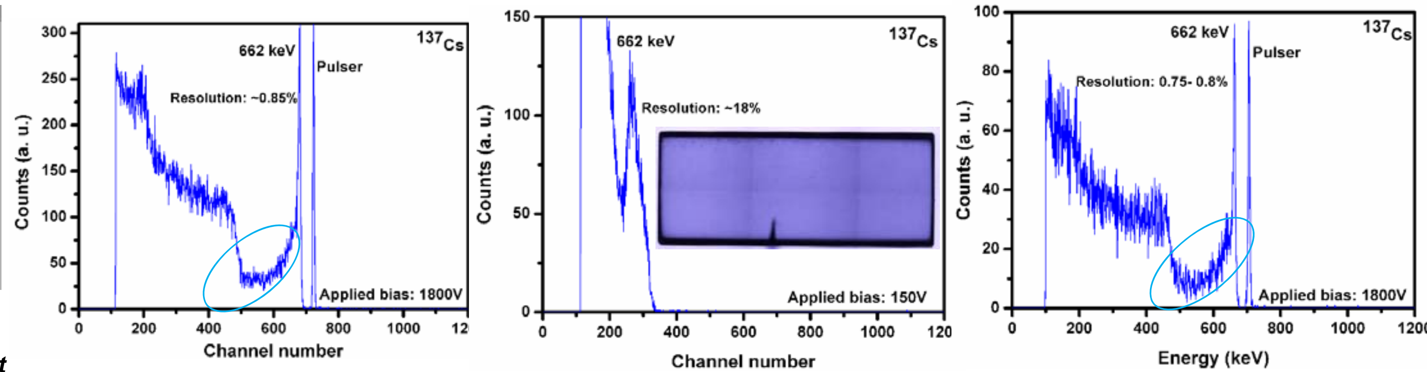
X-ray response mapping using ALS beamline



Peak intensity and peak position map for the $Cd_{0.9}Zn_{0.1}Te_{0.98}Se_{0.02}$ planar detector of dimensions 11.5x7.7x2.55 mm^3, under the bias voltage of 250 V. Inset shows typical spectrum under the bias of 50V.

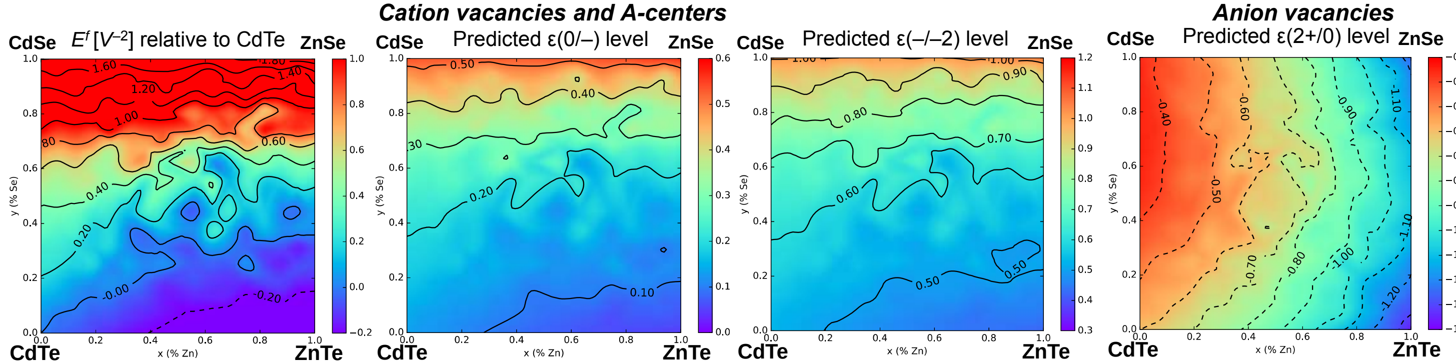
Spatial charge collection uniformity is very high.



Pulse height spectrum from ^{137}Cs source of the Frisch grid detector fabricated from as-grown $Cd_{0.9}Zn_{0.1}Te_{0.98}Se_{0.02}$ ingot by THM. The inset shows the IR transmission picture of the detector. The detector dimensions: ~5x5x12.3 mm^3. Length of Frisch grid ~8mm.

The sharp as-measured spectra from as-grown CZTS ingot shows very high quality nature of the CZTS material. Low voltage operation indicates the presence of very low defects.

Theoretical models are being developed over the entire quaternary composition space to identify changes in point defect concentrations and the location of their states within the band gap



Se decreases (Zn increases) cation vacancy solubility; acceptor states are deeper in the band gap with increasing Se content

Impurity analyses

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6N purity CZT 1 (raw material)

Element	Concentration [ppb at]
Cr	<3
Fe	34
Ni	<5
Cu	<15
Sn	<45
Pb	<2

6N purity CZT 2 (raw material)

Element	Concentration [ppb at]
Cr	<3
Fe	110
Ni	<4
Cu	<8
Sn	<30
Pb	<2

6N purity $Cd_{0.9}Zn_{0.1}Te_{0.98}Se_{0.02}$ grown by THM

Ingot #1

Element	Concentration [ppb at]
Cr	<20
Fe	42
Ni	<4
Cu	22
Sn	<100
Pb	10

Ingot #2

Element	Concentration [ppb at]
Cr	36
Fe	42
Ni	16
Cu	<4
Sn	<100
Pb	11

Future plan for this year (2018)

1. Seeded growth of 2 inch diameter ingot to enhance grain size.
2. Unseeded growth of 3 inch diameter ingot.
3. Synthesis of CdSe from 7N purity Cd and 6N purity Se.

Acknowledgments

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