BNL-101614-2013-CP

Post-Growth Annealing of CdZnTe Crystals: An Analysis of Defect-Structures and Opto-Electronic Properties

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Presented at the 2013 SPIE Optics + Photonics
August 25-29, 2013
San Diego, CA

August 2013

Nonproliferation and National Security Department

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2013 SPIE Optics + Photonics

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Post-growth annealing of CdZnTe crystals: an analysis of defect-structures and opto-electronic properties

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August 28, 2013

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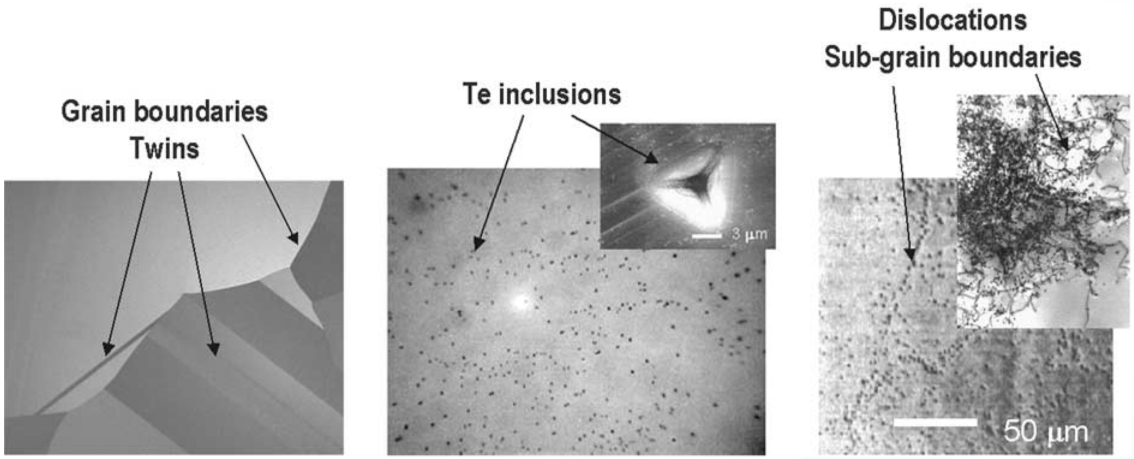
Outline

- **Goal:** Investigate post-growth annealing to improve the performance of CZT detectors
- **Experimental results and discussions**
  - Origin and nature of star-like defects after Cd annealing
  - Resistivity change before and after annealing
  - Low-temperature photoluminescence measurement before and after annealing
- **Summary**

Background and motivation

Material quality is inextricably linked to supply, performance and cost of large-volume CdZnTe (CZT) gamma-ray detectors

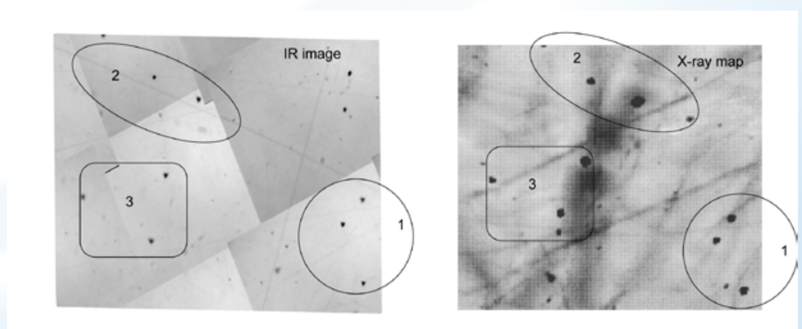
- Different material defects, e.g., tellurium inclusions, dislocations, grain boundaries and sub-grain boundaries, are found in typical CZT crystals



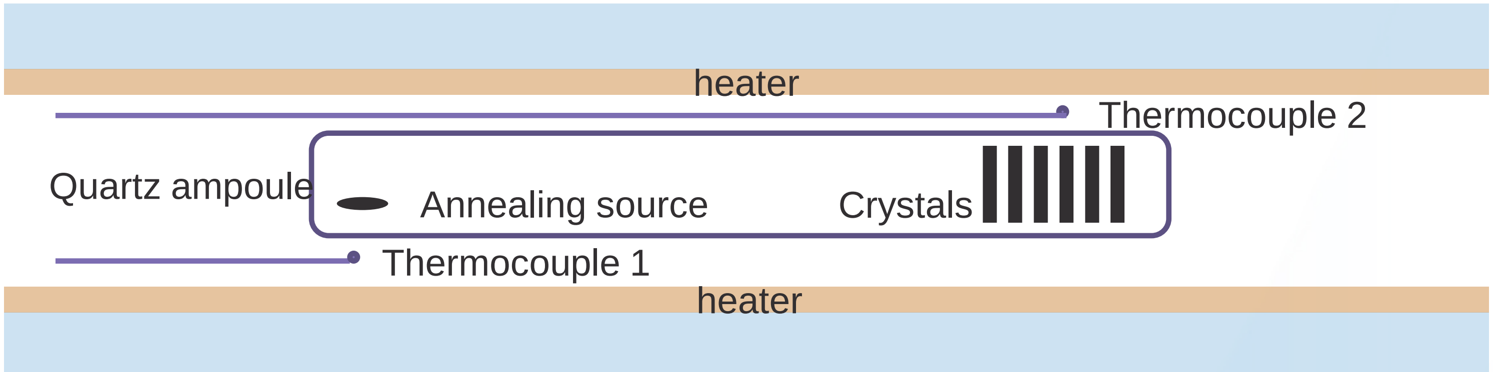
(Csaba Szeles, IEEE transactions on nuclear science, 51, 1242, 2004)

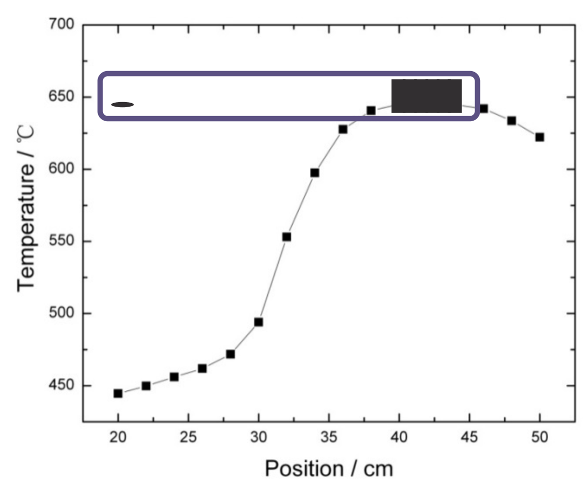
- These material defects play an important role in determining the performance of CZT detectors

An example

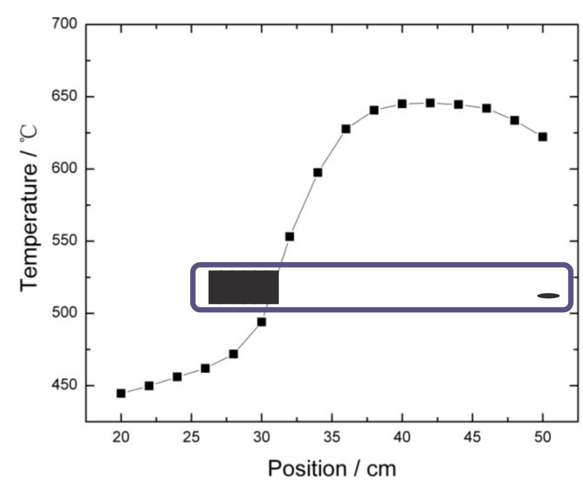


Post-growth annealing — A controllable and reproducible way to address the challenge





Uniform temperature field



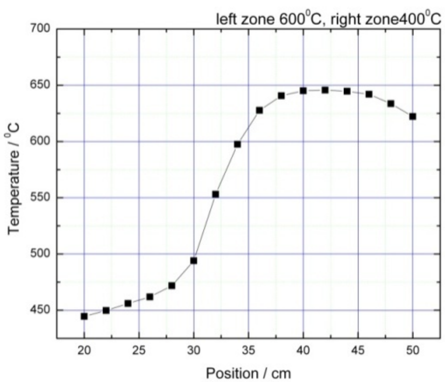
Temperature gradient field

Facilities for annealing study

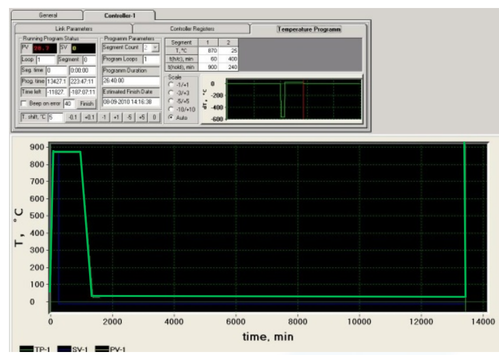
Two-zone annealing furnace

Single-zone annealing furnace # 1

Single-zone annealing furnace # 2



Temperature profile of the annealing furnace (two-zone)

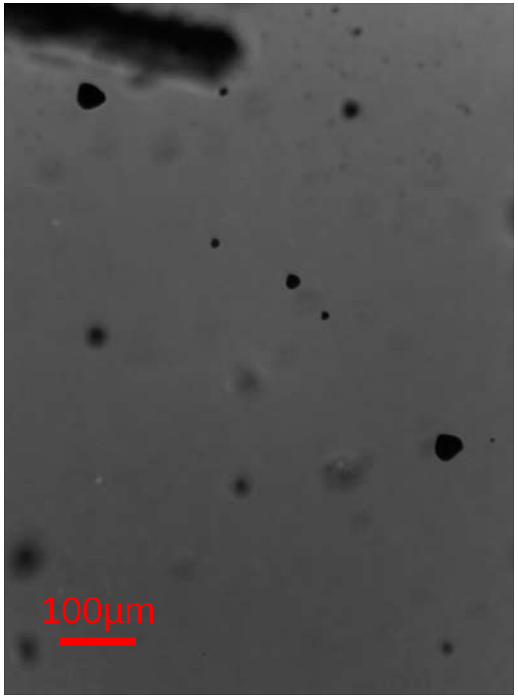


Customized computer-controlling interface

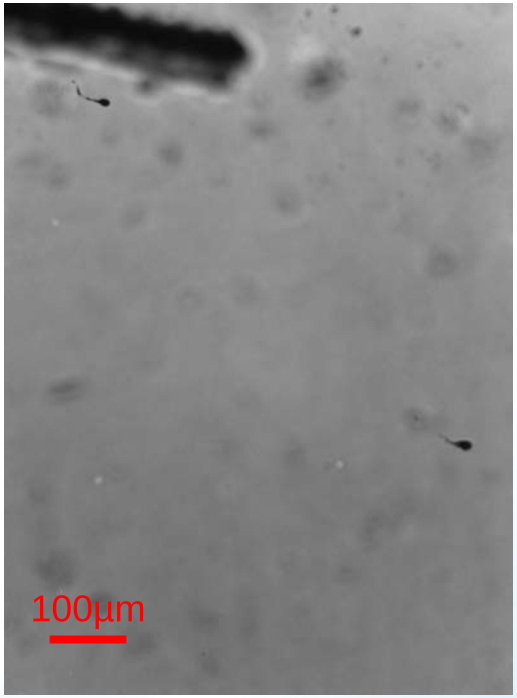
Sealed quartz tubes for annealing experiments

Our previous work demonstrated that the post-growth annealing in Cd vapor helps to remove Te inclusions

Low high

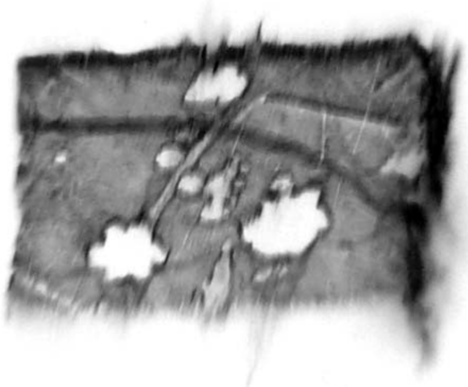


Low high



- Large Te inclusions --- migrate to high temperature side
- Small Te inclusions --- eliminated by the diffusion of external Cd atoms into CZT and their chemical bonding with Te inclusions

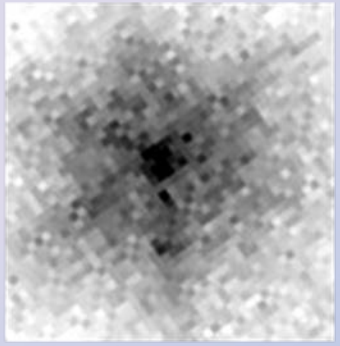
However, ‘star-like’ defects were formed in CdTe, CdZnTe and CdMnTe after the annealing in Cd vapor



White beam X-ray diffraction topography (WBXDT) image

‘Star-like’ defects are often observed in Cd annealed CdTe, CdZnTe and CdMnTe crystals. Such ‘star-like’ defects deteriorate the uniformity of charge transport.

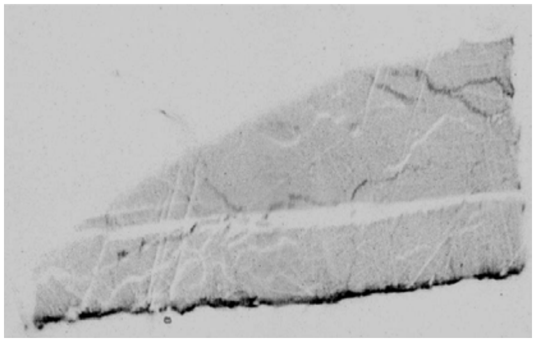
Optical image of etch pits

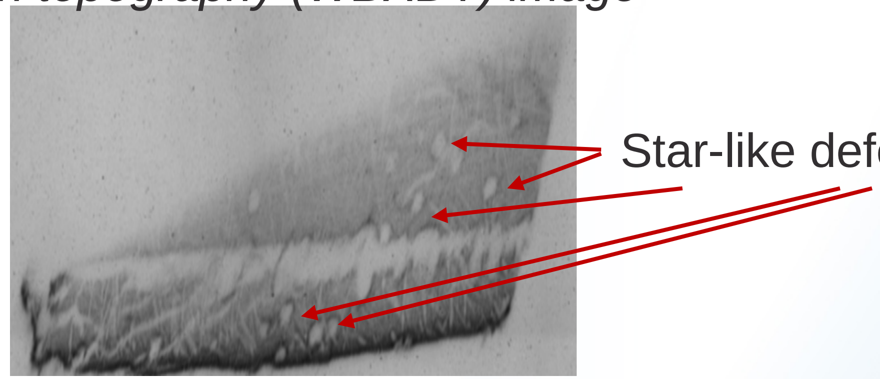


X-ray response map

Star-like defects were observed after high, medium and low temperature Cd annealing

White beam X-ray diffraction topography (WBXDT) image

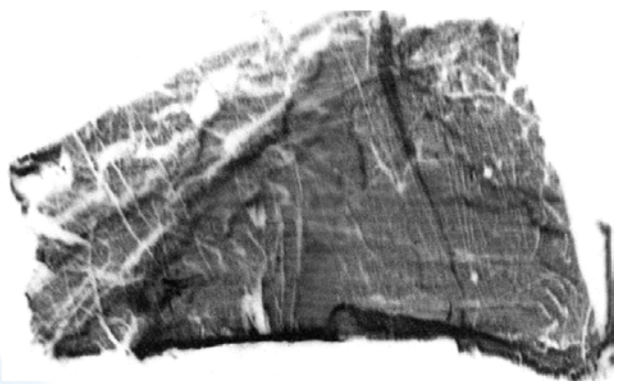


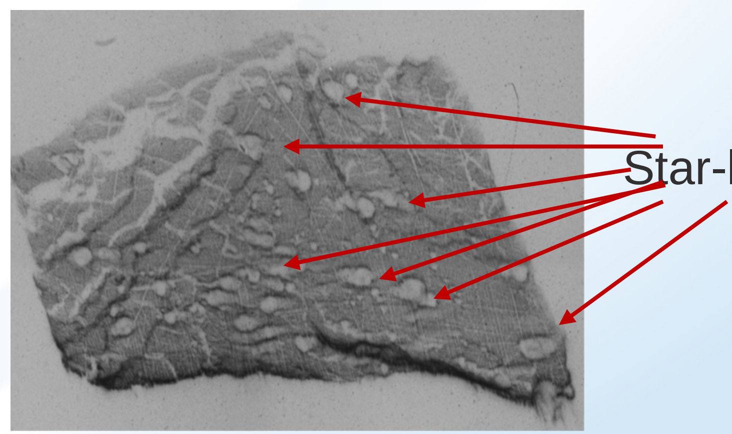


Before annealing

After annealing

(770 ℃, 2 hours, Cd overpressure)





Before annealing

After annealing

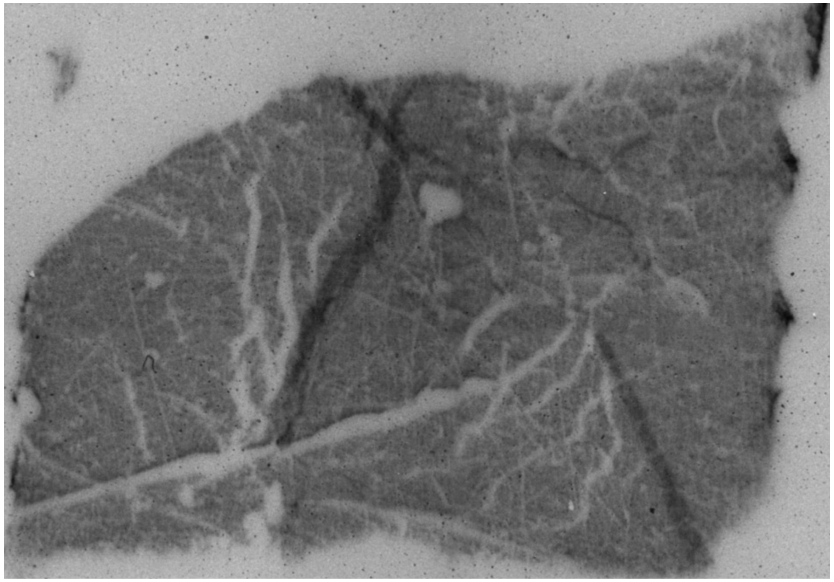
(510 ℃, 60 hours, Cd overpressure)

What's the origin of star-like defects?

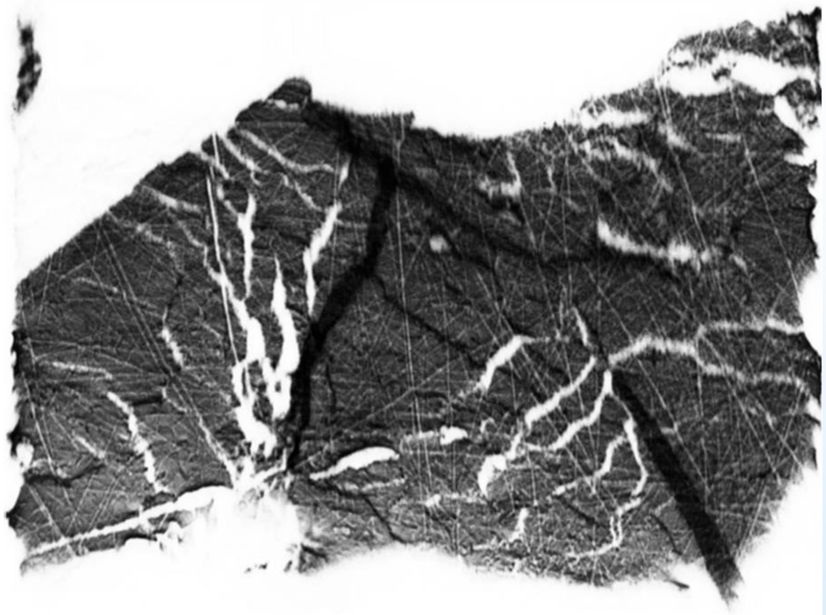
Possibly, the star-like defects are results of the movement, consolidation and reactions of the dislocations surrounding the inclusions (punching dislocations), which are driven by the heat release and the pressure release when eliminating large-size Te inclusions during annealing.

However, sizes of 'star-like' defects are much larger (100 times) than those of Te-rich inclusions and the concentration of 'star-like' defects is much lower than that of Te-rich inclusions before annealing.

Cd annealing at the temperature lower than the melting point of Te, 449 ℃



Before annealing



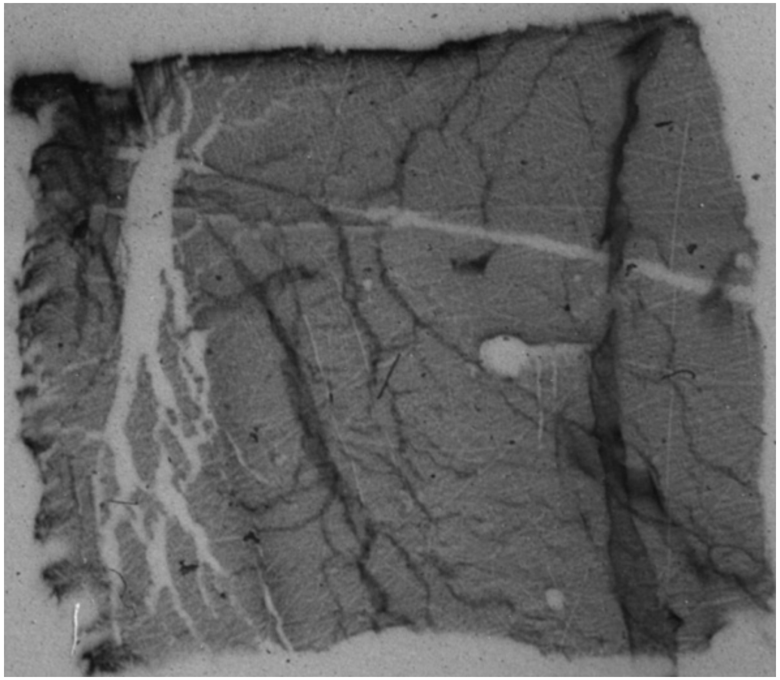
After annealing

(375 ℃, 100 hours)

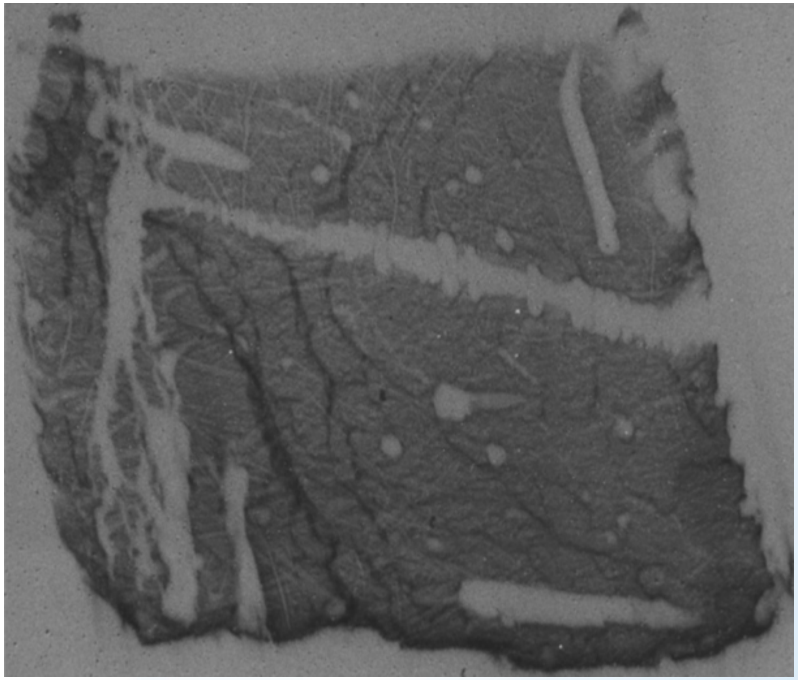
No star-like defects were observed when the annealing temperature is lower than the melting point of Te.

Cd annealing at the temperature slightly higher than the melting point of Te, 449 ℃

WBXDT images



Before annealing



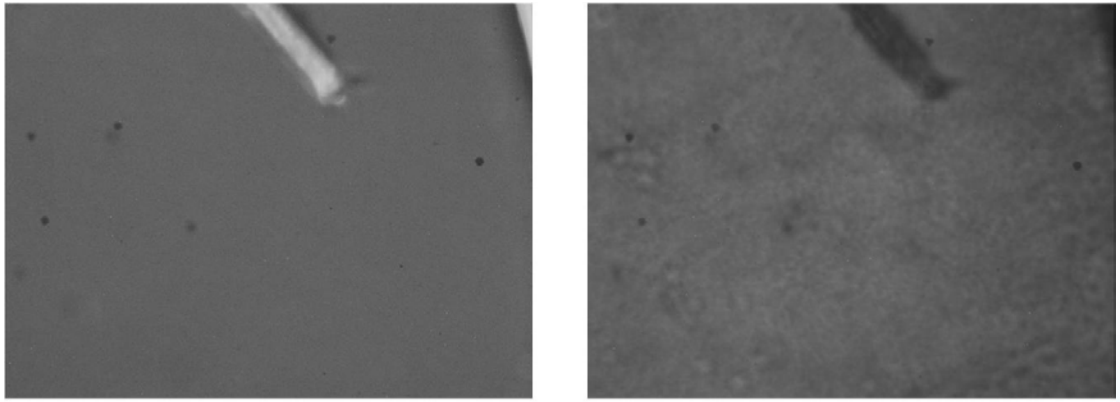
After annealing

(480 ℃, 20 hours)

Star-like defects appear even when the annealing temperature is slightly higher than the melting point of Te.

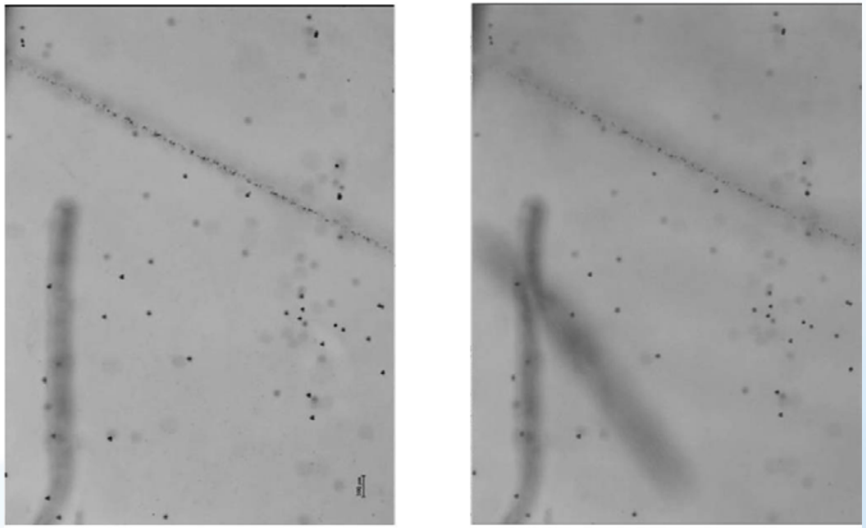
Distribution of Te inclusions after Cd annealing in low-temperature range

(375 ℃ for 100 hours)



Before annealing IR images After annealing

The concentration of Te inclusions were not reduced at both annealing conditions.

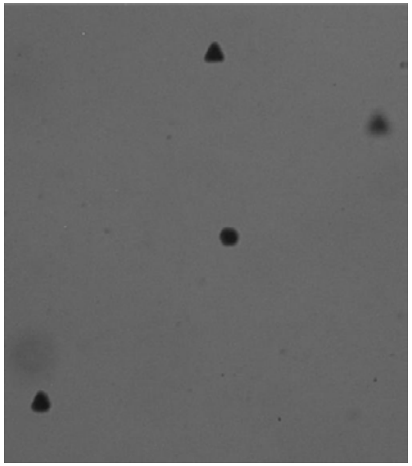


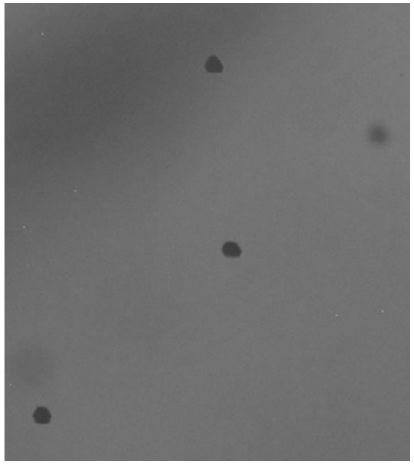
Before annealing IR images After annealing

(480 ℃ for 20 hours)

Shape change of Te inclusions after Cd annealing in low-temperature range

IR images

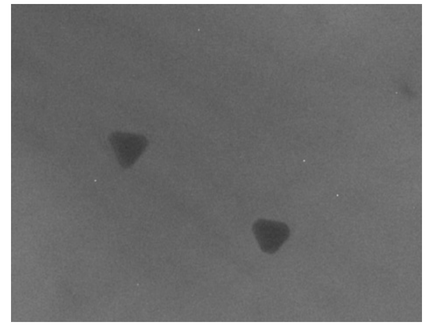


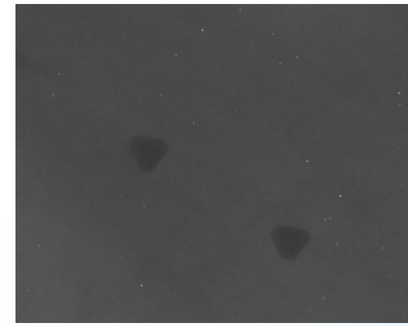


Before annealing After annealing
(480 ℃ for 20 hours)

Shape change reflects the melting- solidification process

IR images





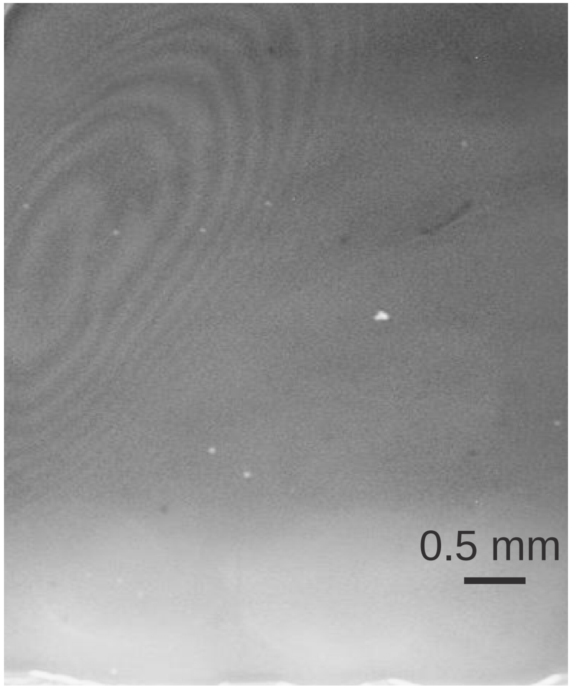
Before annealing After annealing

(375 ℃ for 100 hours)

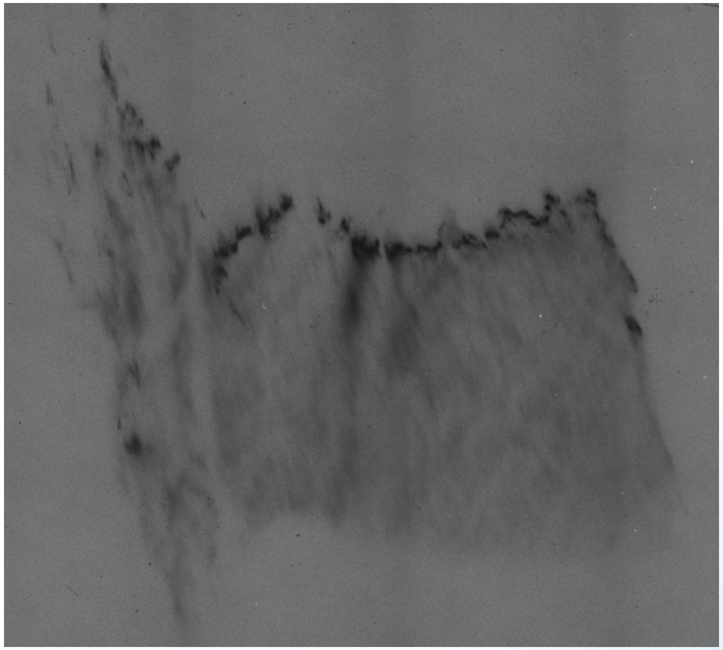
No shape change

The formation of the ‘star-like’ defects occurs at the initiation of the reaction process between the diffused Cd- and molten Te-inclusions, considering that the volume of Te inclusions stay almost unchanged while many ‘star-like’ defects already had formed.

Cd annealing on crystals free of Te inclusions (grown by modified floating-zone method)



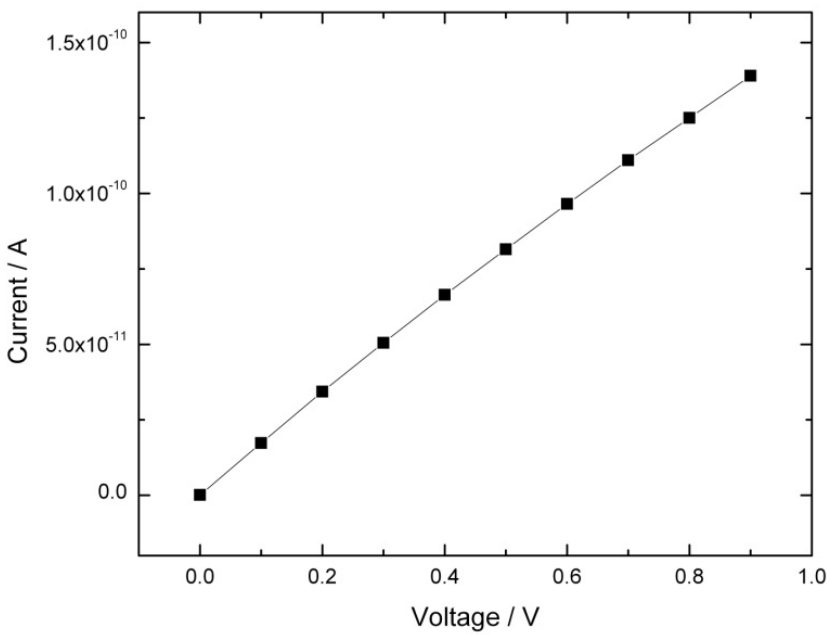
IR microscopy of a typical FZ-grown CMT crystal. The crystal is free of Te inclusions.



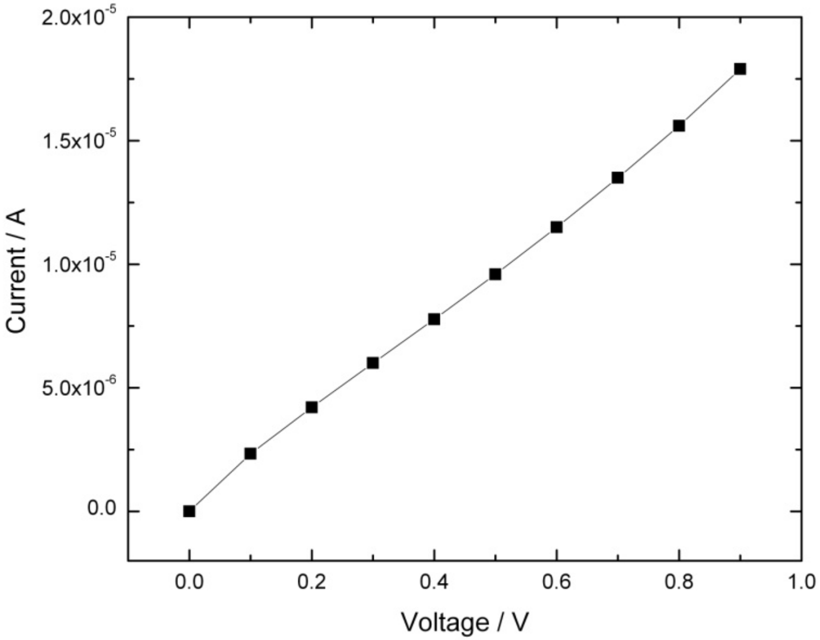
WBXDT images of a CMT crystal free of Te inclusion (FZ-grown) before and after annealing in Cd vapor at 570 ℃.

No ‘star-like’ defects were observed after Cd annealing! It confirms that this type of defects are related to inclusions.

We reported that the resistivity was lowered after one-step Cd annealing



Before annealing



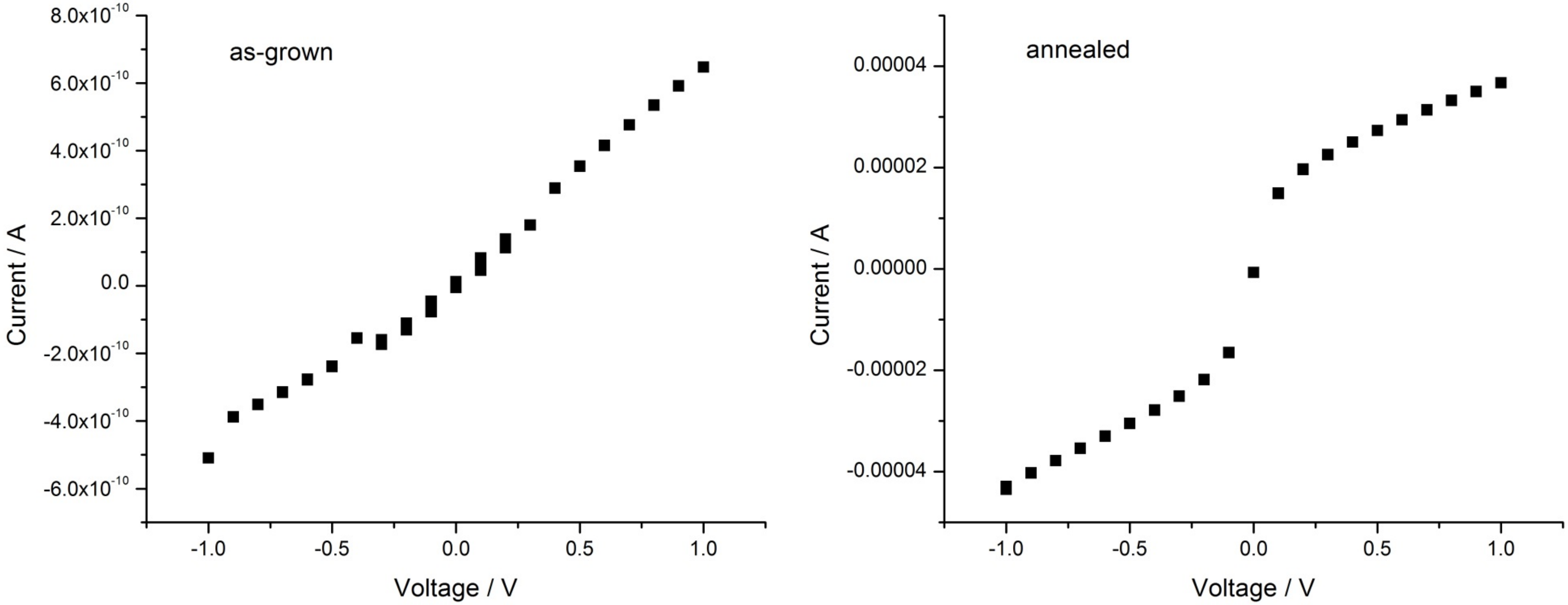
After annealing

Annealing in Cd vapor

The resistivity was reduced from 10^{11} Ωcm to 10^{6} Ωcm after the annealing in one-step Cd vapor. (even this step can eliminate Te inclusions).

Then what is the change of resistivity after one-step Te annealing?

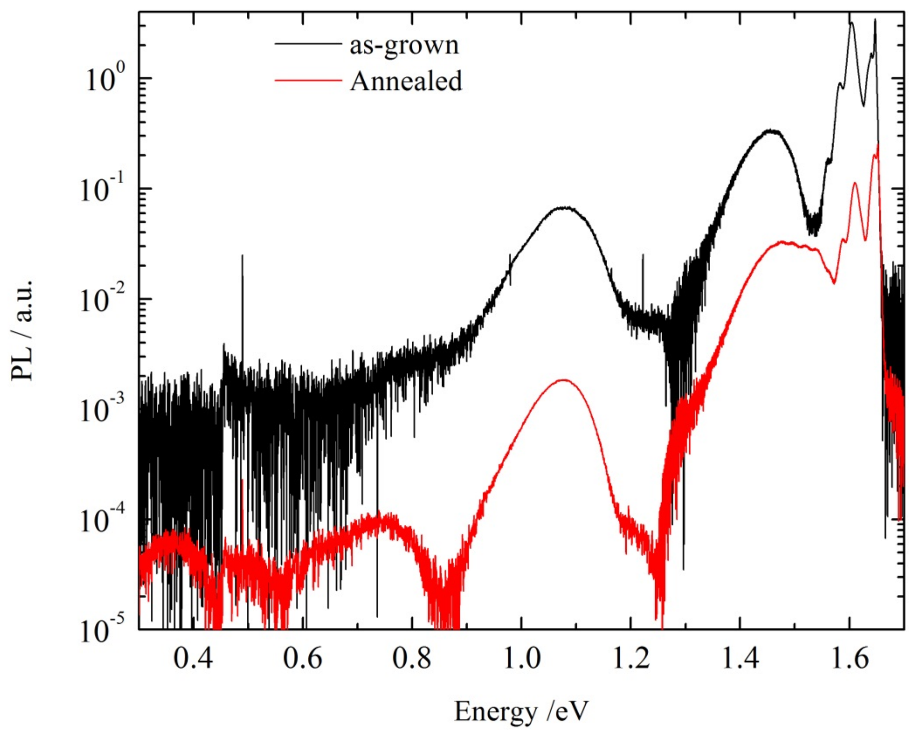
Resistivity change during one-step Te annealing



Annealing in Te vapor, 610 ℃

The resistivity of CZT can also be lowered from 10^{11} Ωcm to 10^{6} Ωcm after one-step annealing in Te vapor, similarly with the case of annealing in Cd vapor. What's the reason for such change?

4.2 K photoluminescence (PL) spectrum of as-grown and Te-annealed CZT



After annealing in Te vapor, we observed two new deep peaks including

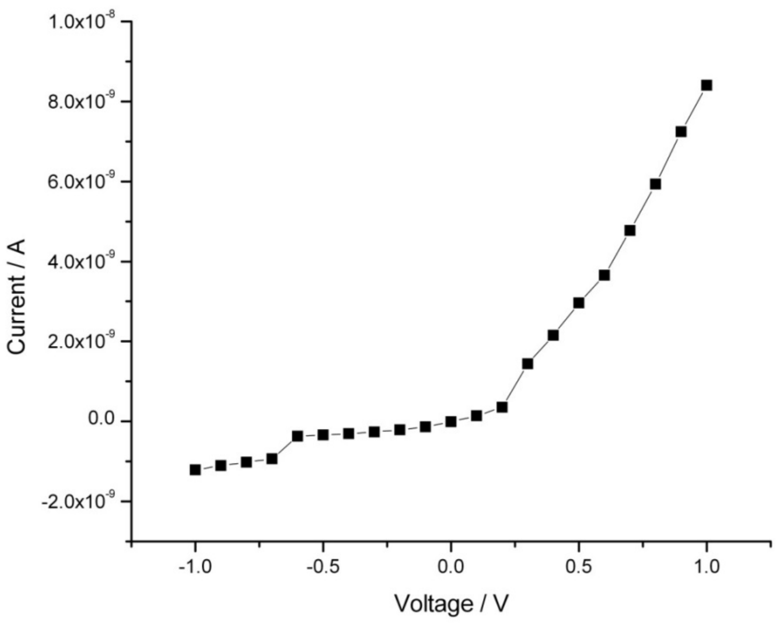
(1) a new peak at 0.743 eV, which corresponds to Te antisite, and
(2) a new peak at 0.367 eV, the origin and role of which are still unclear at this moment.

Is the deep donor Te antisite really responsible for high resistivity, i.e., compensating the shallow acceptor Cd vacancies and pinning the Fermi level?

We see Te-antisite-related peak in Te annealed crystals and didn't observe it in as-grown ones.

Two possible approaches to maintain high resistivity

- Two-step annealing, i.e., Cd annealing to eliminate Te inclusions, followed by Te annealing to recover the resistivity
- One-step annealing with suitable Cd + Zn pressure control



The resistivity keeps relatively high after the annealing (10^9 $\Omega\cdot$cm), given suitable Cd pressure and Zn pressure control.

Summary

- Star-like defects were observed after Cd annealing in Bridgman-grown and THM –grown crystals with typical distribution of Te inclusions.
- Such star-like defects were only observed when the annealing temperature is higher than the melting point of Te.
- Star-like defects were absent in the crystals free of Te inclusions, which were grown by modified floating-zone method.
- Either one-step Cd annealing or one-step Te annealing lowers the resistivity.
- Two new deep-level peaks, at 0.743 eV and 0.367 eV respectively, appear in the 4.2 K PL spectrum of CZT after Te annealing.

Acknowledgement

This work was supported by U.S. Department of Energy, Office of Defense Nuclear Nonproliferation Research and Development, DNN R&D.

Thank you for your attention!