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Defect Analysis of CdZnTe Crystals and the Related Thermal Annealing Studies

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Defect analysis of CdZnTe crystals and the related thermal annealing studies

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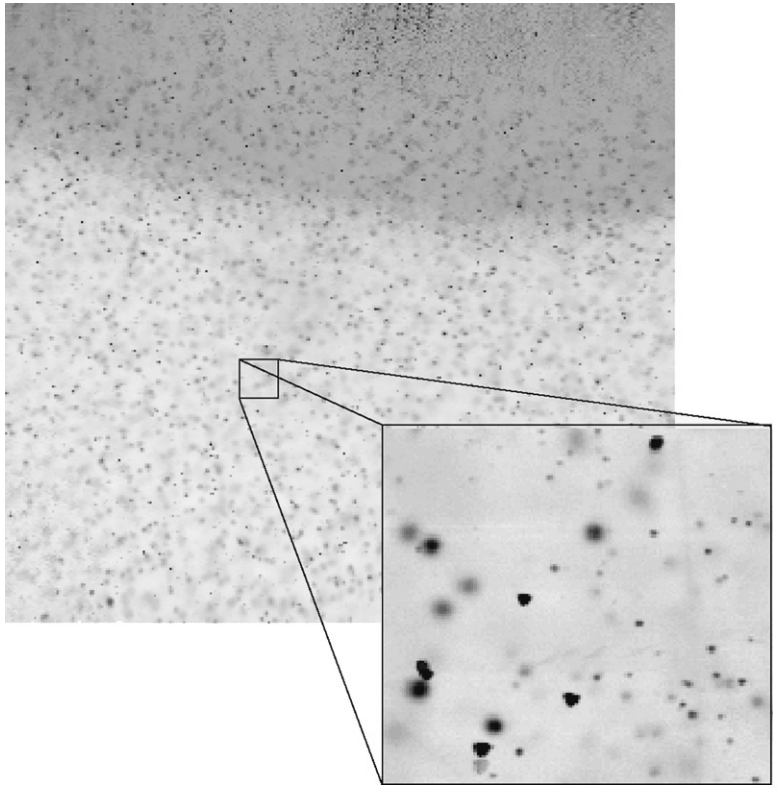
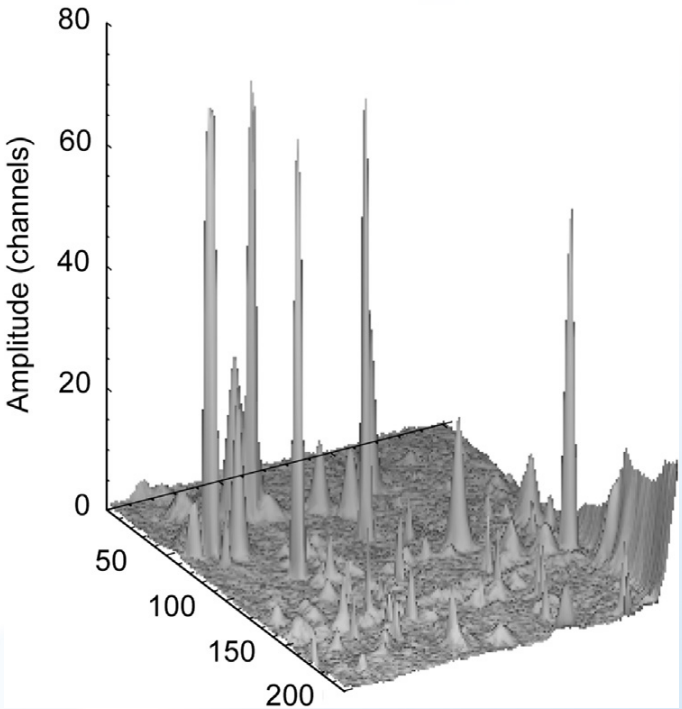
Outline

- **Goal:** Investigate effects of post-growth annealing on the defects in detector-grade CdZnTe crystals
- **Experimental results and discussions**
  - Evolution of Te inclusions during annealing
  - Origin and nature of star-like defects after Cd annealing
  - Effects on carrier trapping
- **Summary**

Background and motivation

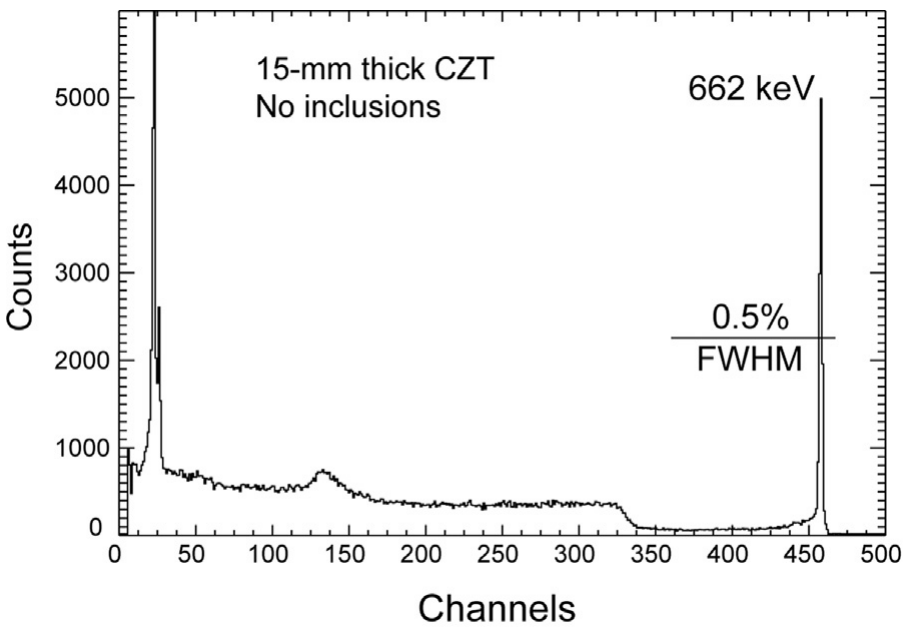
Te inclusions in as-grown CdZnTe (CZT) have been a 'hot' topic in the past several years!

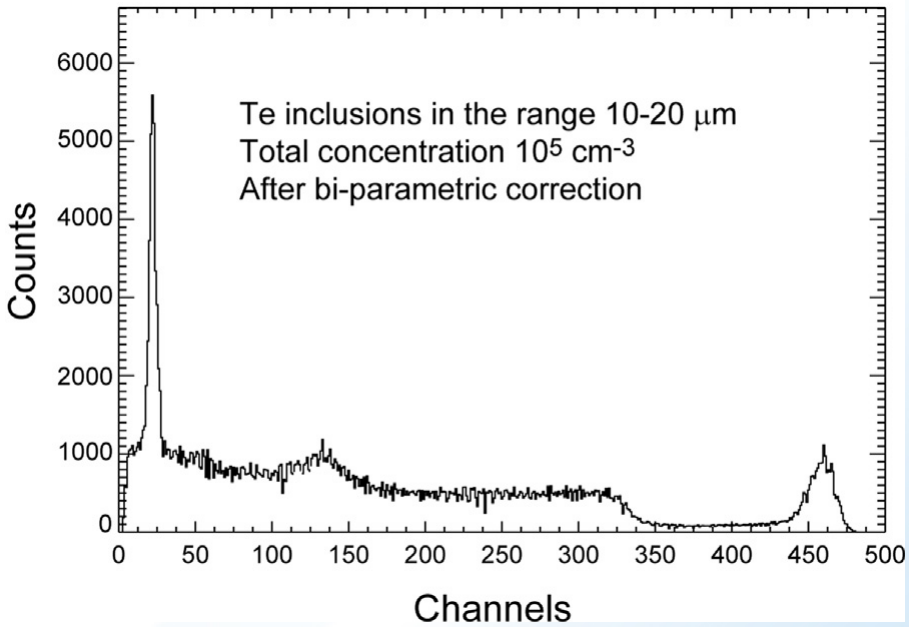




2D and 3D high spatial-resolution
X-ray response map

Effects of Te inclusions on device performance of large-volume CZT gamma-ray detectors



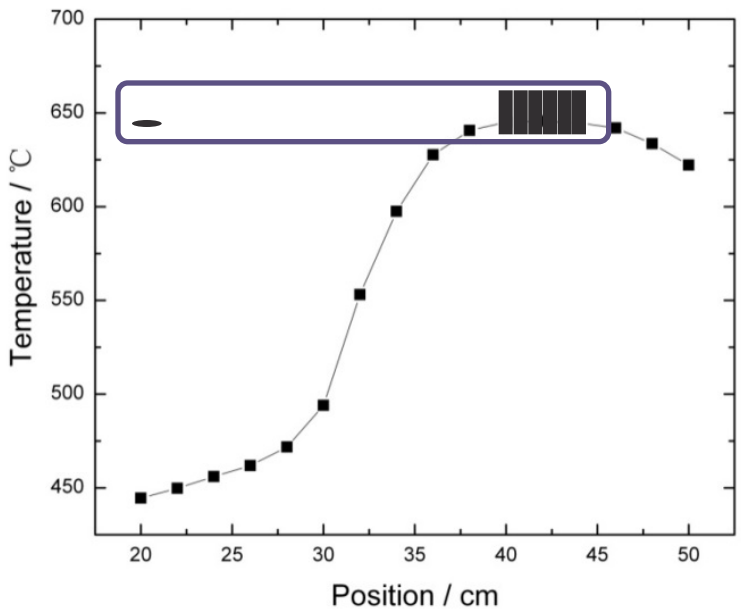


We have clear evidence that their presence is inextricably linked to performance, availability and cost of large-volume CZT gamma-ray detectors*

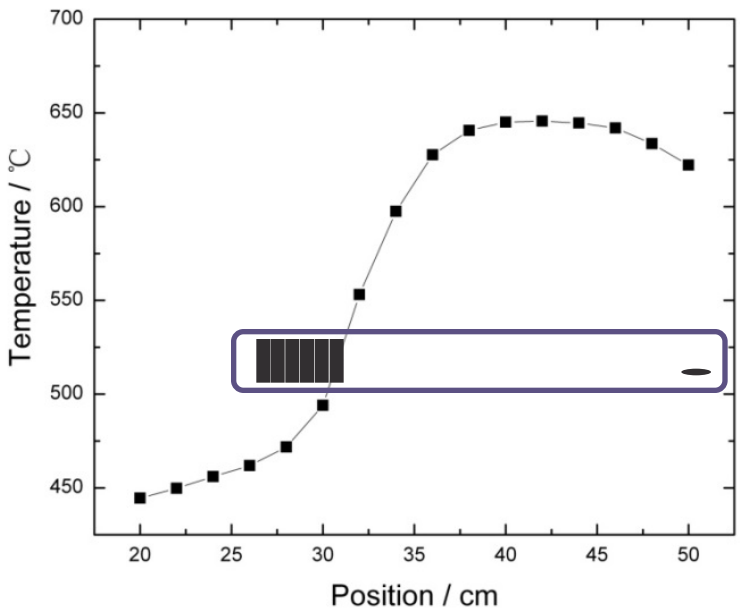
* Bolotnikov, et al., Journal of Crystal Growth, 379, 46 (2013)

Why is post-growth annealing a promising approach to improve CZT quality?

The starting point: people want to get rid of Te inclusions of as-grown CZT crystals through post-growth annealing without creating new trapping centers

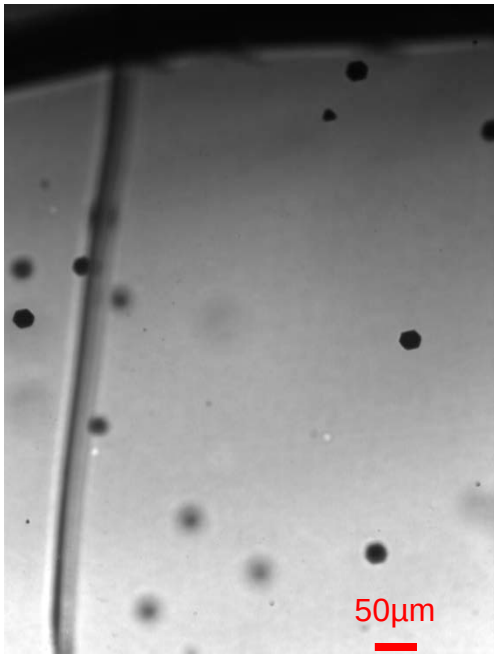


Uniform temperature field

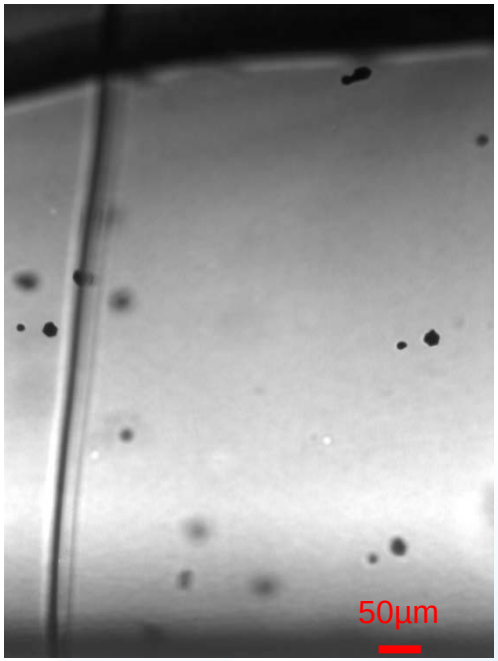


Temperature gradient field

Migration of Te inclusions were observed during post-growth annealing in a temperature gradient field



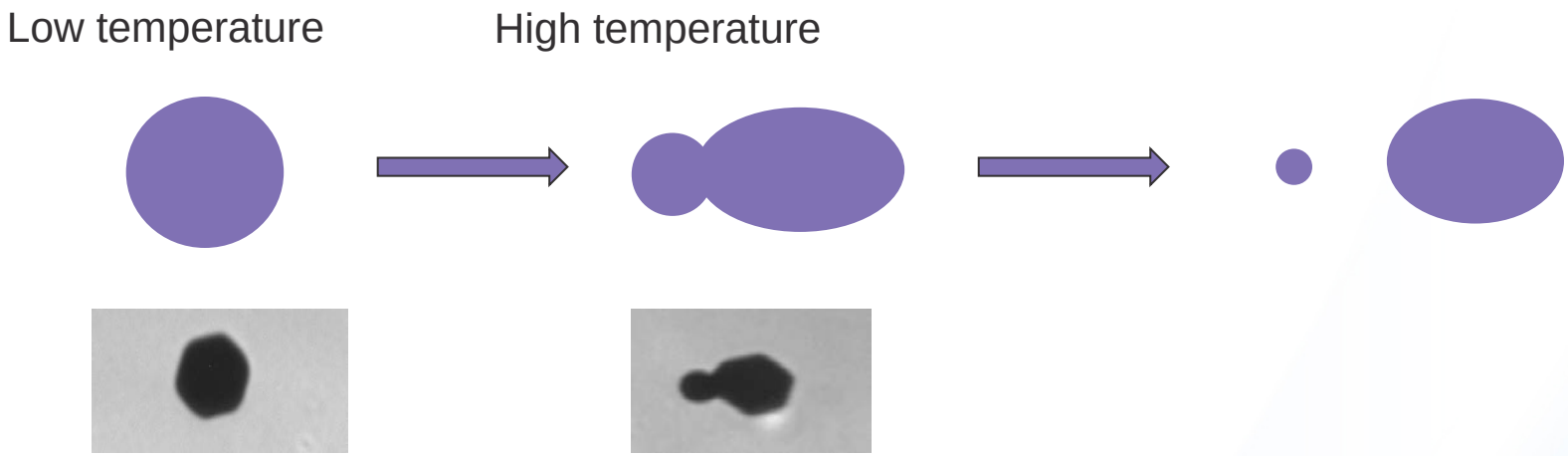
Before annealing



After annealing

Condition: 700 ℃, temp. gradient 10 ℃ /cm, Cd overpressure

General picture of migration behavior of Te inclusions



Three processes:

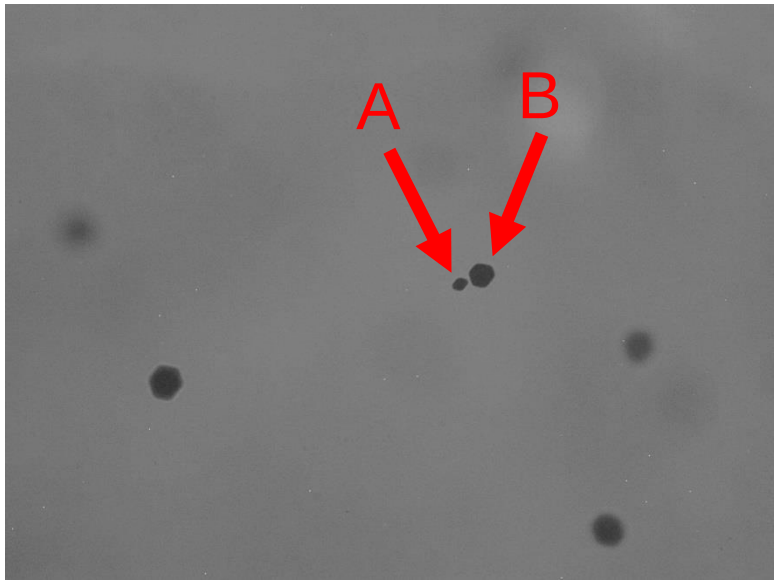
(1) Dissolution of CZT at the hot surface
(2) Molecular and thermal diffusion through the melt Te
(3) Crystallization at the cold surface

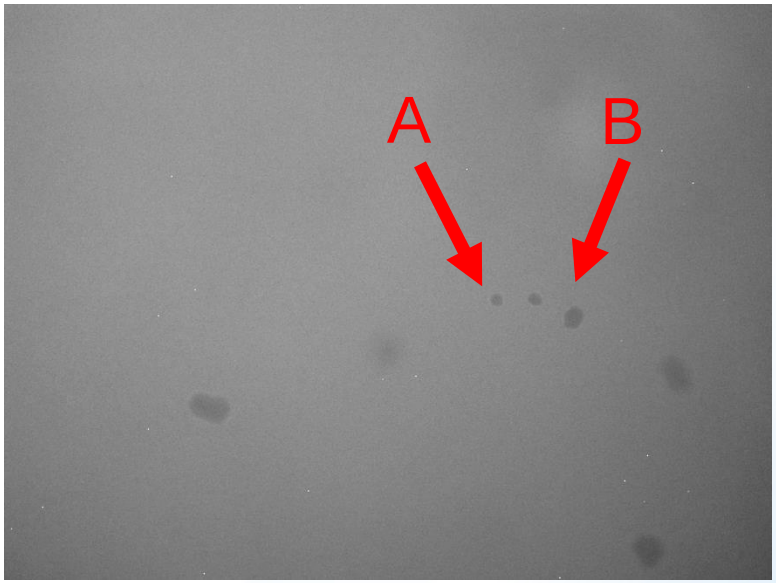
Migration rate can be described as

$$v = \frac{1}{\rho_s}\frac{D_l C^{sat}}{1+D}\left[\left(C^{\frac{1}{sat}}\frac{dC^{sat}}{dT} - \alpha\right)\nabla T_l - \frac{\varepsilon^*}{L}\right]$$

* Olander et al., technical report, U. of California

However, not all Te inclusions have the same migration behavior under the temperature-gradient annealing





The temperature gradient across inclusion A and inclusion B should be same since both inclusions are close to each other.

Why does one inclusion (inclusion B) migrate and the other one (inclusions A) not?

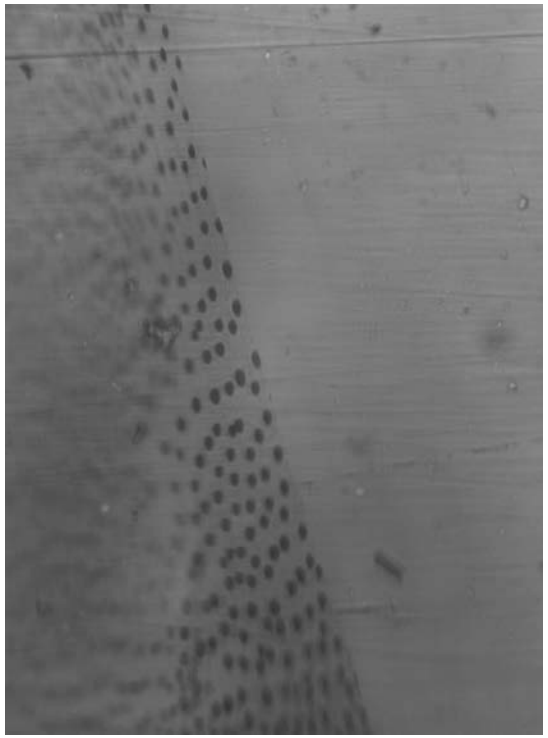
Interface kinetics consideration during the migration process of Te inclusions

At the threshold conditions, the temperature difference across the inclusion is just sufficient to meet the requirement of critical undersaturation for dissolution at the hot interface and critical supersaturation for growth at the cold surface. As a result, we get the minimum inclusion size for migration:

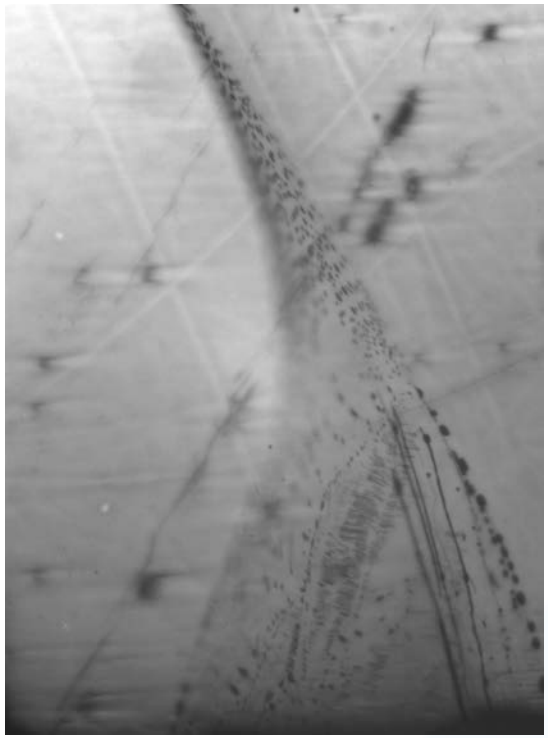
$$L_{min} = \frac{\varepsilon^*}{\left(C^{\frac{1}{sat}} \frac{dC^{sat}}{dT} - \alpha\right) \nabla T_l}$$

Physically, the existence of L_{min} is so small that the critical-sized nuclei for growth and dissolution cannot be sustained.

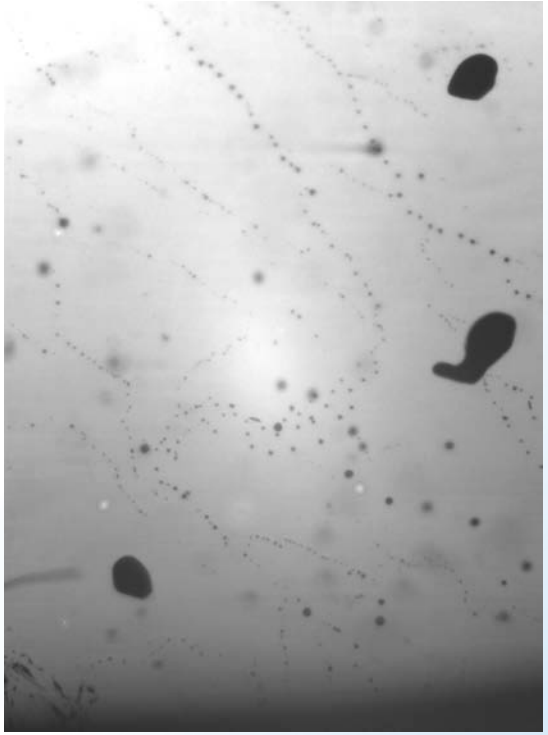
In reality, Te inclusions can distribute along different structural defects



Twin boundaries



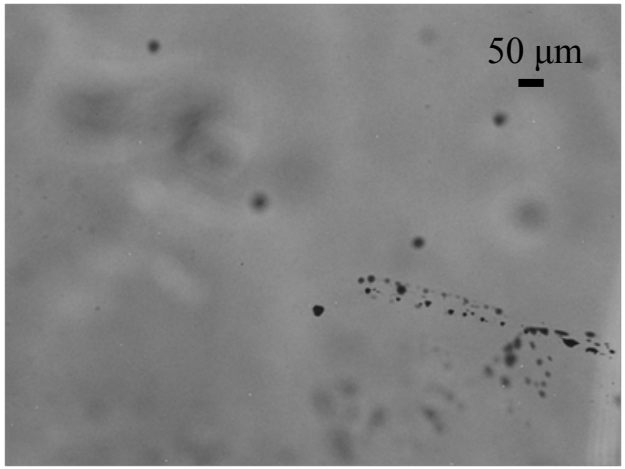
Grain boundaries



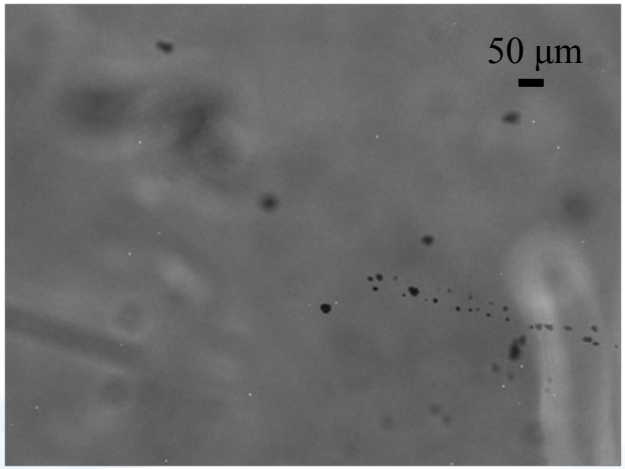
Sub-grain boundaries

These structural defects make the migration behaviors of Te inclusions more complicated!

Behavior of Te inclusions at grain boundaries during the annealing with a temperature gradient



Before annealing



After annealing

Thermo-migration behavior of Te inclusions also depends on their specific locations within the CdZnTe matrix. Even larger-size Te inclusions do not migrate across grain boundaries.

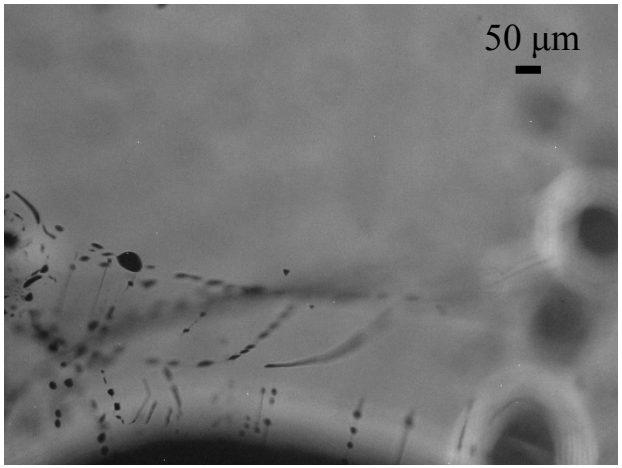
It implies that grain boundaries may have some a strong trapping effect on the migration of Te inclusions.

Annealing condition: 580 ℃, temp. gradient 35 ℃/cm, Cd overpressure

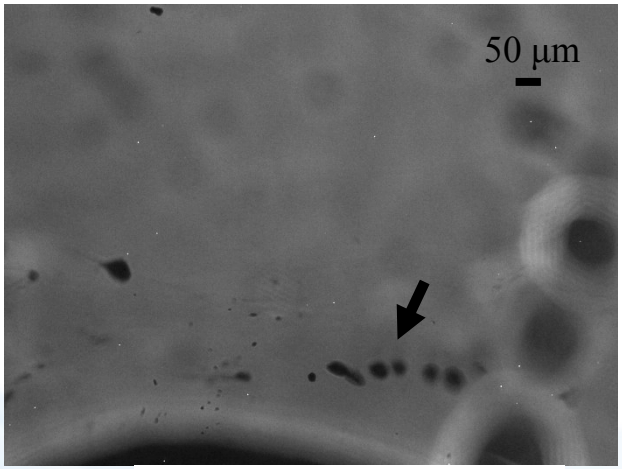
Low temperature High temperature

Formation of Te inclusions at grain boundaries

Low temperature High temperature



before the annealing



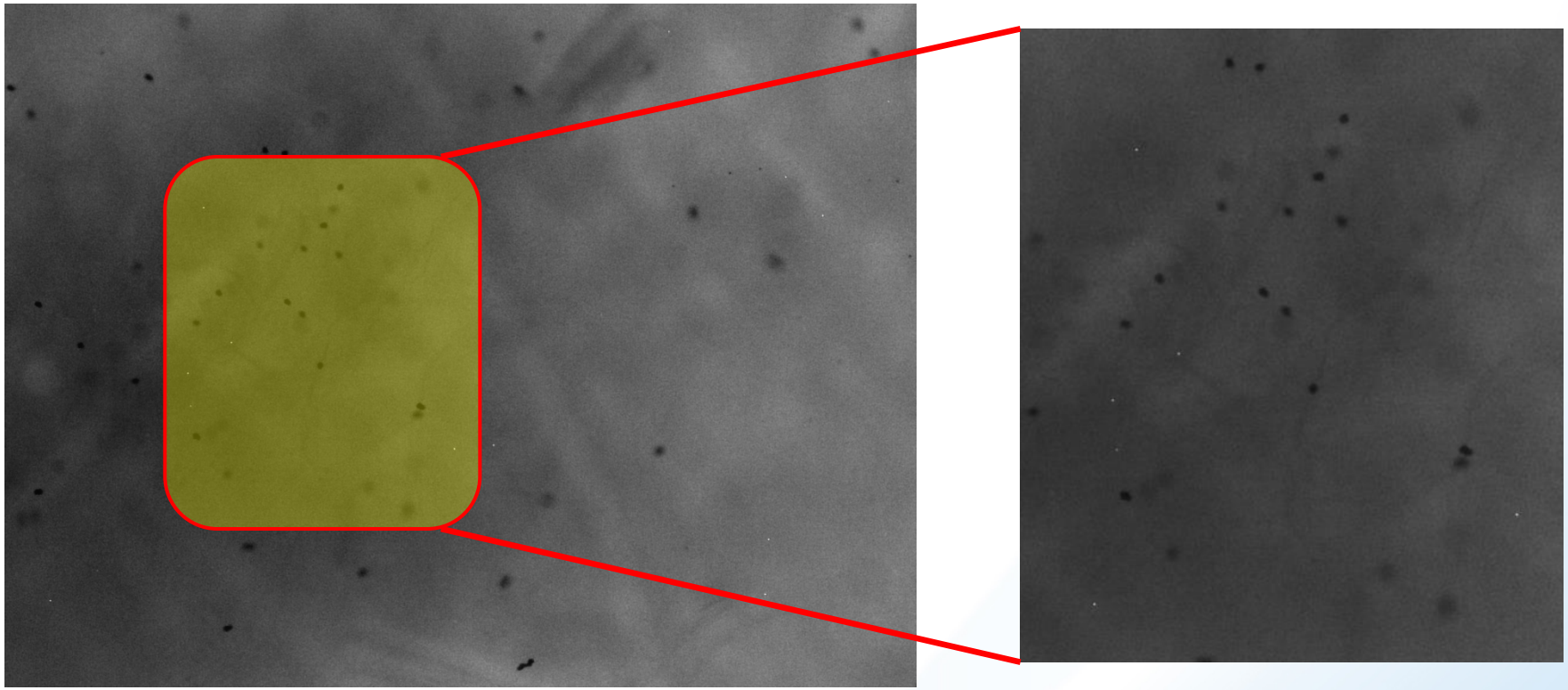
after the annealing

IR transmission images

Some Te inclusions were newly formed during the annealing, possibly because the grain boundaries provide the fast-diffusing channels to getter excess Te atoms.

Annealing condition: 580 ℃, temp. gradient 35 ℃/cm, Cd overpressure

Effects of sub-grain boundaries/dislocation networks

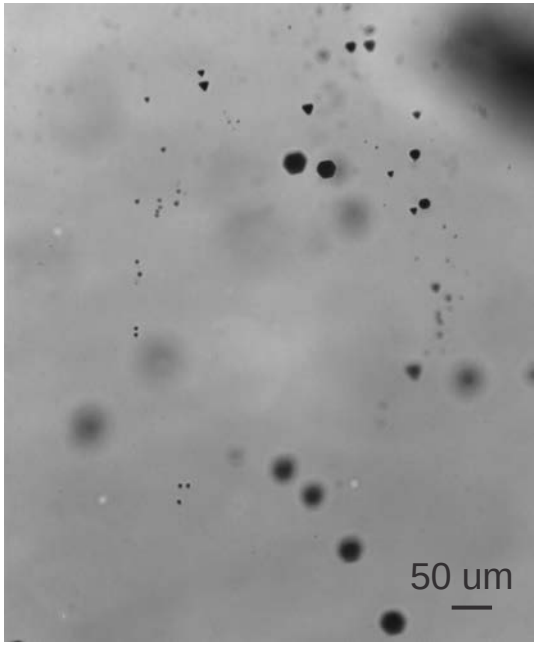


Temperature gradient 45 ℃ /cm

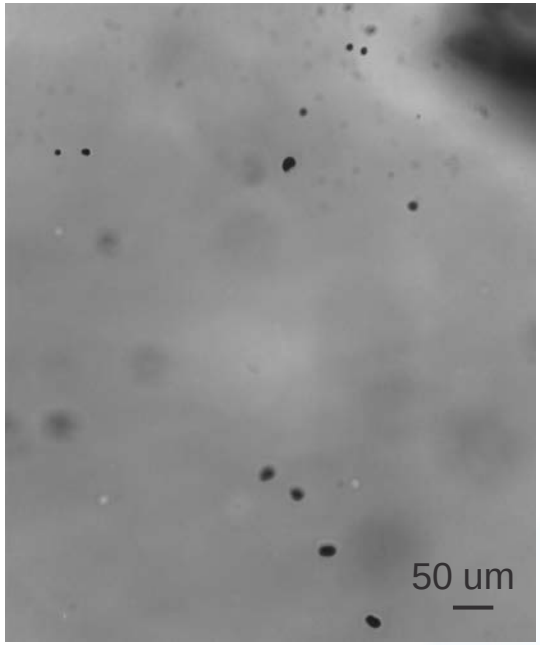
Some line patterns appeared after Cd annealing, where Te inclusions are not able to migrate. These patterns are sub-grain boundaries dislocation networks decorated by diffused Cd, which trap Te inclusions and prevent their migration.

Track the reduction efficiency of Te inclusions during post-growth annealing

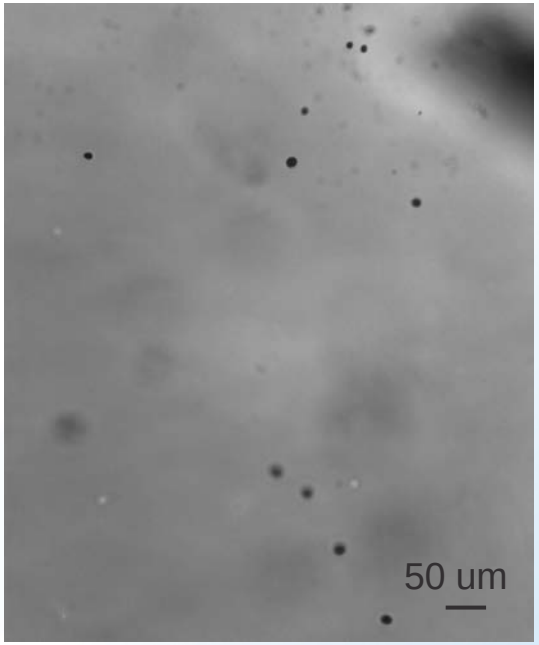
Multiple annealing steps were used



Before annealing

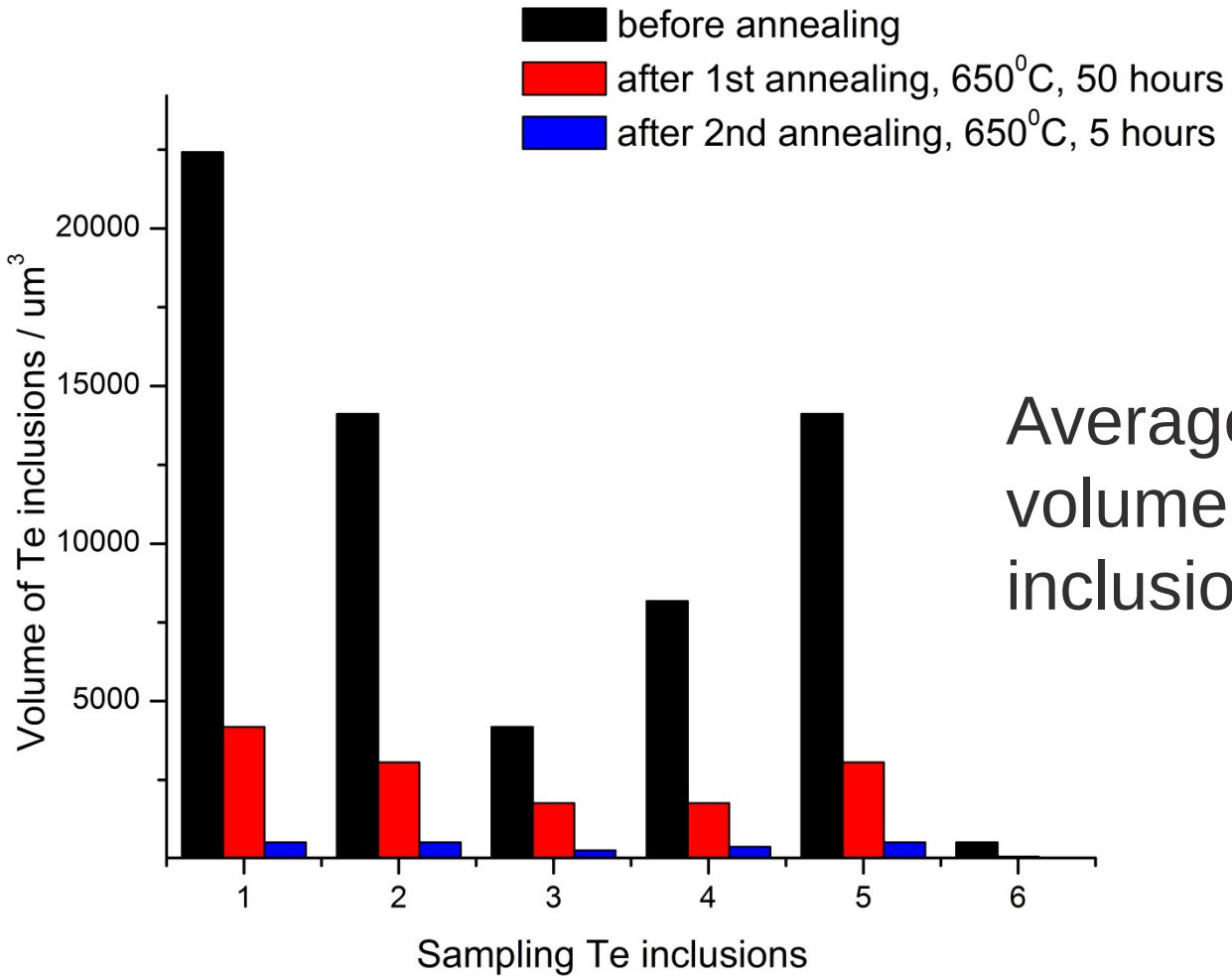


1st annealing
650 ℃, 50 hours



2nd annealing
650 ℃, 5 hours

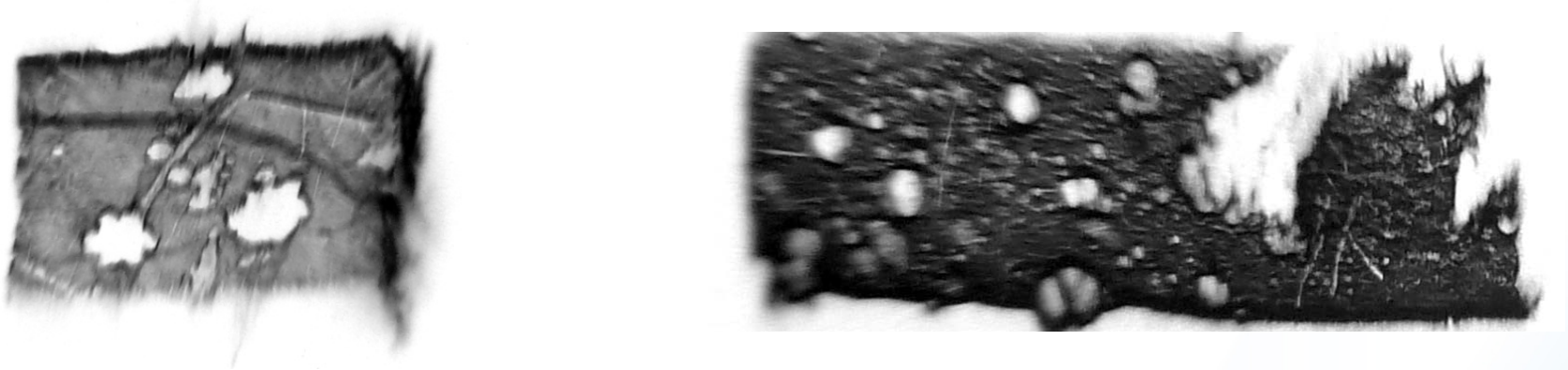
Changes of volume of Te inclusions



Average reduction in volume of Te inclusions is ~ 78%

Note: All Te inclusions of < 5 μm disappear or become smaller than 1 μm (optical microscope resolution) after annealing

Star-like defects were formed in CdTe, CdZnTe and CdMnTe after the annealing in Cd vapor

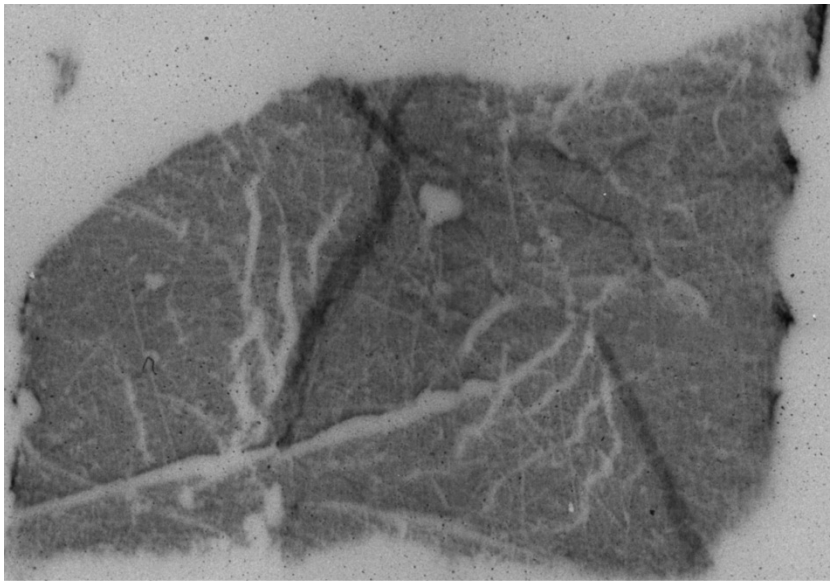


White beam X-ray diffraction topography (WBXDT) image

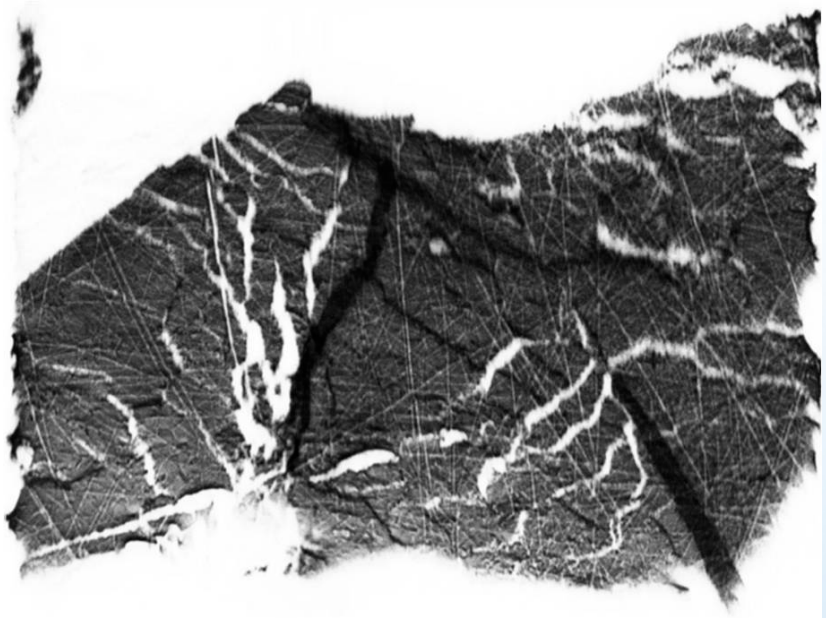
Star-like defects are often observed in Cd annealed CdTe, CdZnTe and CdMnTe crystals. Such 'star-like' defects deteriorate the uniformity of charge transport.

Optical image of etch pits | *X-ray response map*

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



Before annealing



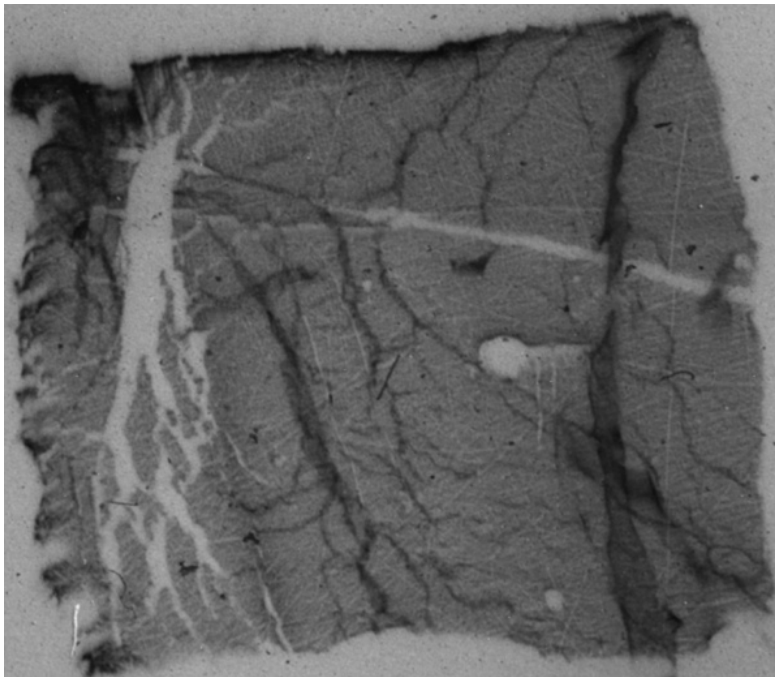
After annealing

(375 ℃, 100 hours)

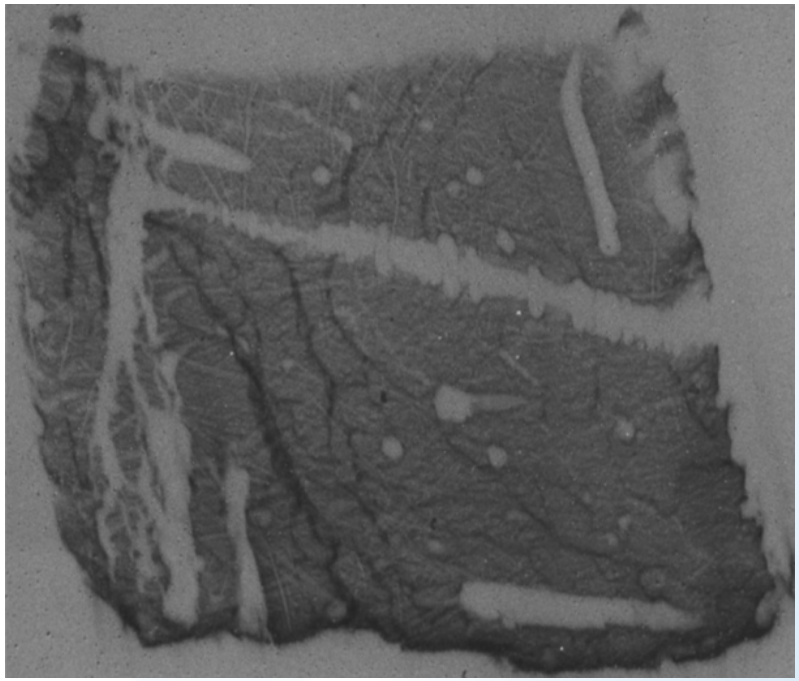
No star-like defects were observed when the annealing temperature is lower than the melting point of Te.

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

WBXDT images



Before annealing

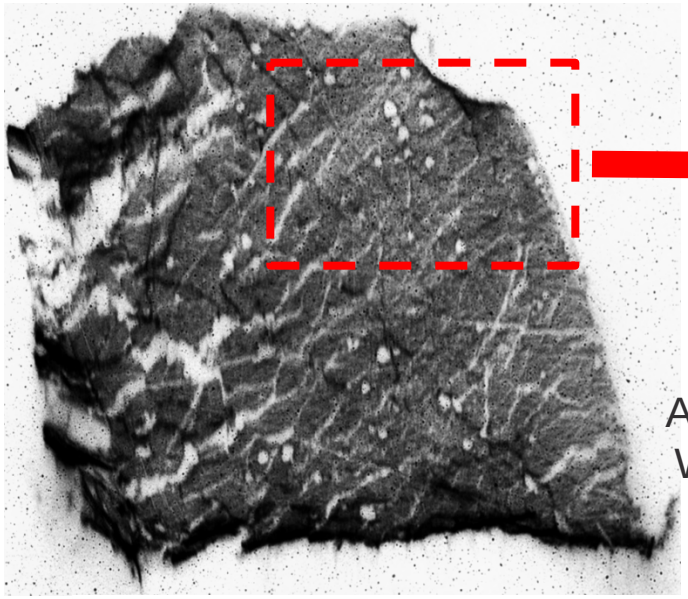


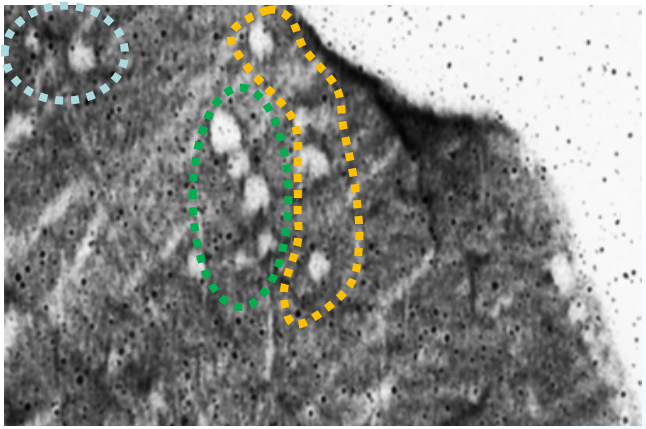
After annealing

(480 ℃, 20 hours)

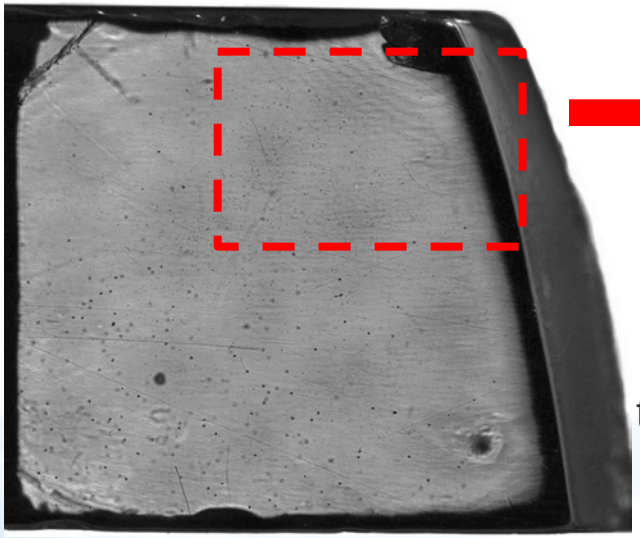
Star-like defects appear even when the annealing temperature is slightly higher than the melting point of Te.

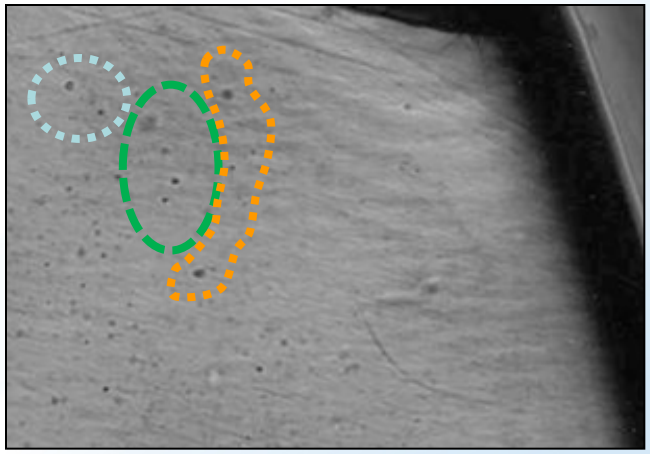
Correlation between star-like defects and Te inclusions





After annealing, WBXDT image





After annealing, IR transmission image

Annealing condition: 470 ℃, 10 hours, Cd vapor

Summary

- Annealing in Cd vapors & under temperature gradient helps to efficiently reduce the density of Te inclusions of different sizes.
- Grain boundaries and sub-grain boundaries have a trapping effect on the migration of Te inclusions during the annealing in a temperature-gradient field.
- Reduction in Te inclusion volumes is about 78% following annealing in Cd vapor at 650 ^{o}C for 50 hours.
- Star-like defects were observed after Cd annealing in Bridgman and THM grown crystals with typical distribution of Te inclusions.
- Correlations were found between Te inclusions, star-like defects and trapping in some regions.

Acknowledgement

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Thank you for your attention!