NELSON MANDELA UNIVERSITY

In situ TEM observation of defect formation in SHI induced tetragonal tracks in monoclinic zirconia

Mike Lee[1], Jacques O'Connell[1] and Vladimir Skuratov[2]

[1]Centre for HRTEM, Nelson Mandela University, Port Elizabeth, South Africa

[2] Flerov Laboratory for Nuclear Research, Joint Institute for Nuclear Research, Dubna, Russia

INTRODUCTION

- Previously reported on the SHI formation of tetragonal tracks as observed in bulk monoclinic zirconia by TEM imaging.

- As far as we are aware, this was the first report and that there were no previous reports of direct imaging of ion tracks in bulk monoclinic zirconia

- In this presentation, we will compare the results for data obtained from TEM images for the room temperature stabilized single ion tetragonal tracks produced in the parent monoclinic zirconia, to the predictions proposed by theoretical models.

- Secondly we will show TEM results for the in situ thermally induced transformation of the tetragonal tracks to the monoclinic phase with the corresponding formation of loop like defects.

- The possible dominant mechanism for this transformation will be proposed.

Properties for bulk zirconia

- The low pressure isomorphs for zirconia are;

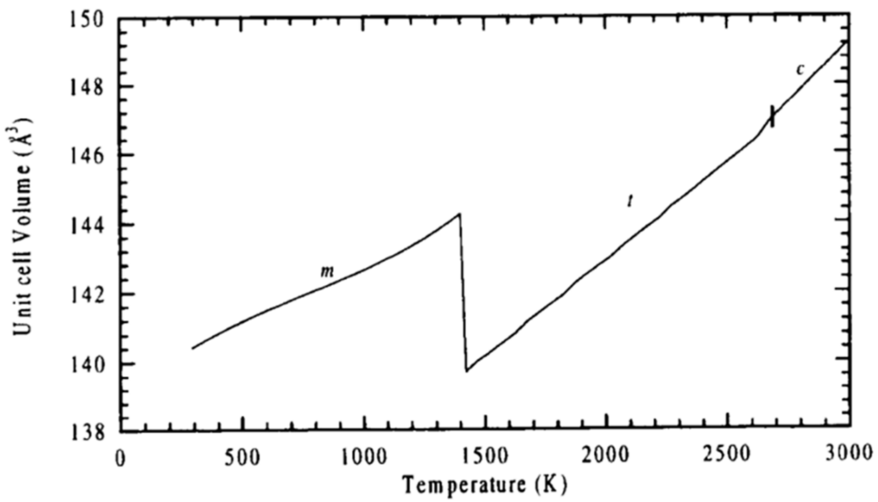
  Monoclinic (m) ⟷ tetragonal (t) ⟷ cubic (c) ⟷ liquid 2800^{0}C

- The m⟷t martensitic transition spreads over a temperature range of 975 - 1200 °C and 1135 - 700 °C during heating and cooling, respectively (thermal hysteresis).

- The phase transformation t ⟷ m results in a <u>shear strain</u> of 16-18% and a <u>volume increase</u> in the order ~5%

- The bulk tetragonal and cubic phases cannot be quenched.

t- and c-zirconia can be stabilized at room temperature by the addition of low valence oxides as CaO, MgO, Y_2O_3 with a resultant increase in oxygen vacancies.



RT stabilization of high temperature zirconia phases

- Pure t-zirconia can be stabilized, at RT, as crystallites having dimensions 3-100 nm which has been reported for the formation of polycrystalline bulk material, thin layers or powders

- Critical size for m $\rightarrow$ t transformation has been described by the Garvie equation

- The room temperature stabilization of cubic crystallites below a critical diameter of 2 nm has been proposed and observed

- Thermal plasma dissociation of zircon grains has been observed to produce plasma dissociated m-and t-zirconia (PDZ) in a glassy silica (SiO_2) matrix on thermal quenching size dependent). (Minnaar et al)

- The mechanism for the formation and stabilization of tetragonal crystallites will depend on the free energy, surface energy, internal strain, lattice strain, point defects, defect clusters and dislocations

- A number of reports have suggested that oxygen vacancies are the dominant mechanism for the stabilization of tetragonal and cubic zirconia.

Formation SHI induced tetragonal tracks for zirconia

- Previous speaker presented introduction into SHI track formation

- Case of monoclinic (m) zirconia the SHI irradiation produces a track containing tetragonal phase segments

- Assume the SHI dissipates energy with resulting melting of material which firstly crystallizes as the cubic phase and finally stabilizes as the tetragonal phase containing a higher concentration of oxygen vacancies. High temperature mobility.

- Most SHI irradiation results for simple binary oxides result in track formation containing defect loops. Possibly no alternative polymorphs.

- Question: Why is the tetragonal phase stabilized and subsequently produces defect loops on annealing?

Experimental

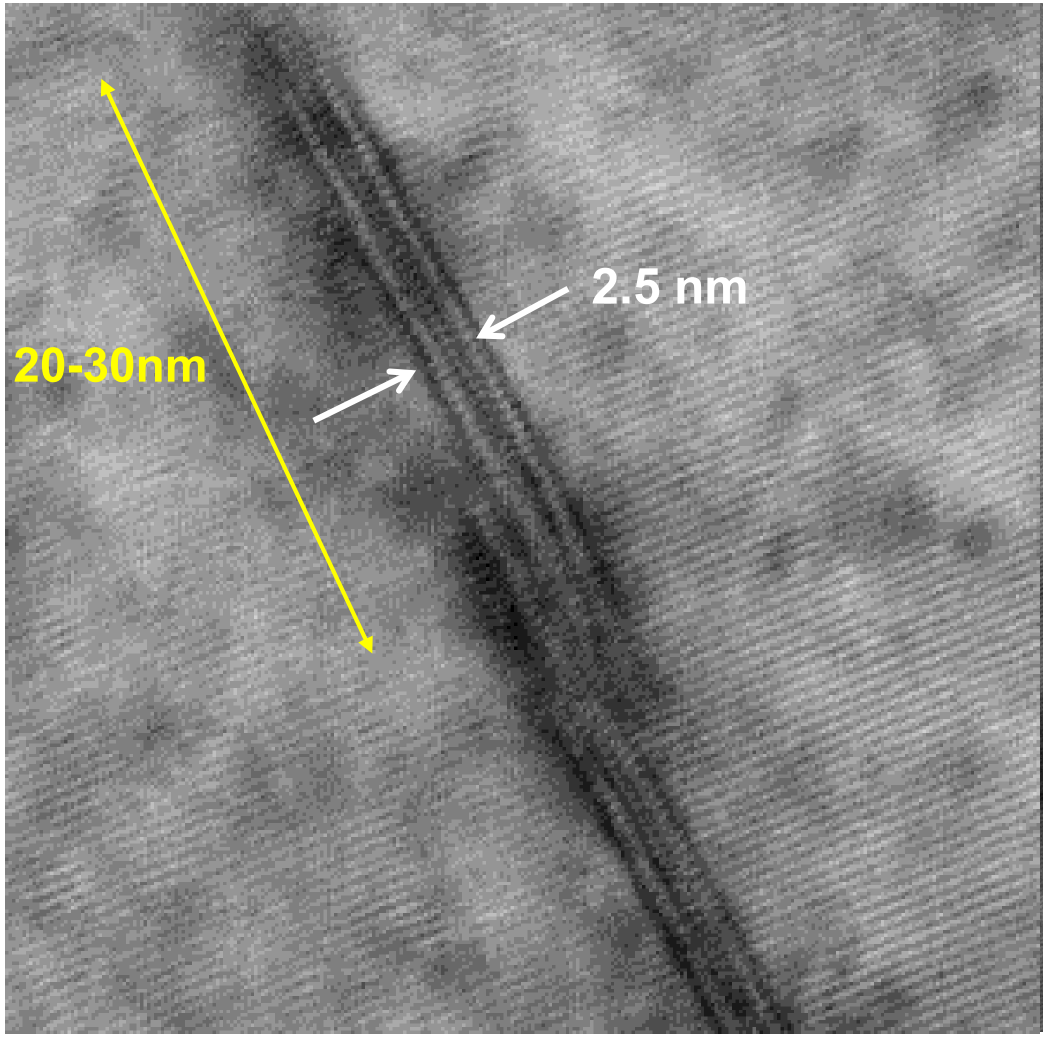
- Natural zirconia was irradiated with 167 MeV Xe ions at the FLNR cyclotron complex in Dubna, Russia, to a fluence of 2×10^{10} cm^{-2} at RT, which is $\perp$ $(100)_m$.

- TEM lamellae were prepared in cross section and plan view geometry using an FEI Helios Nanolab focussed ion beam (FIB).

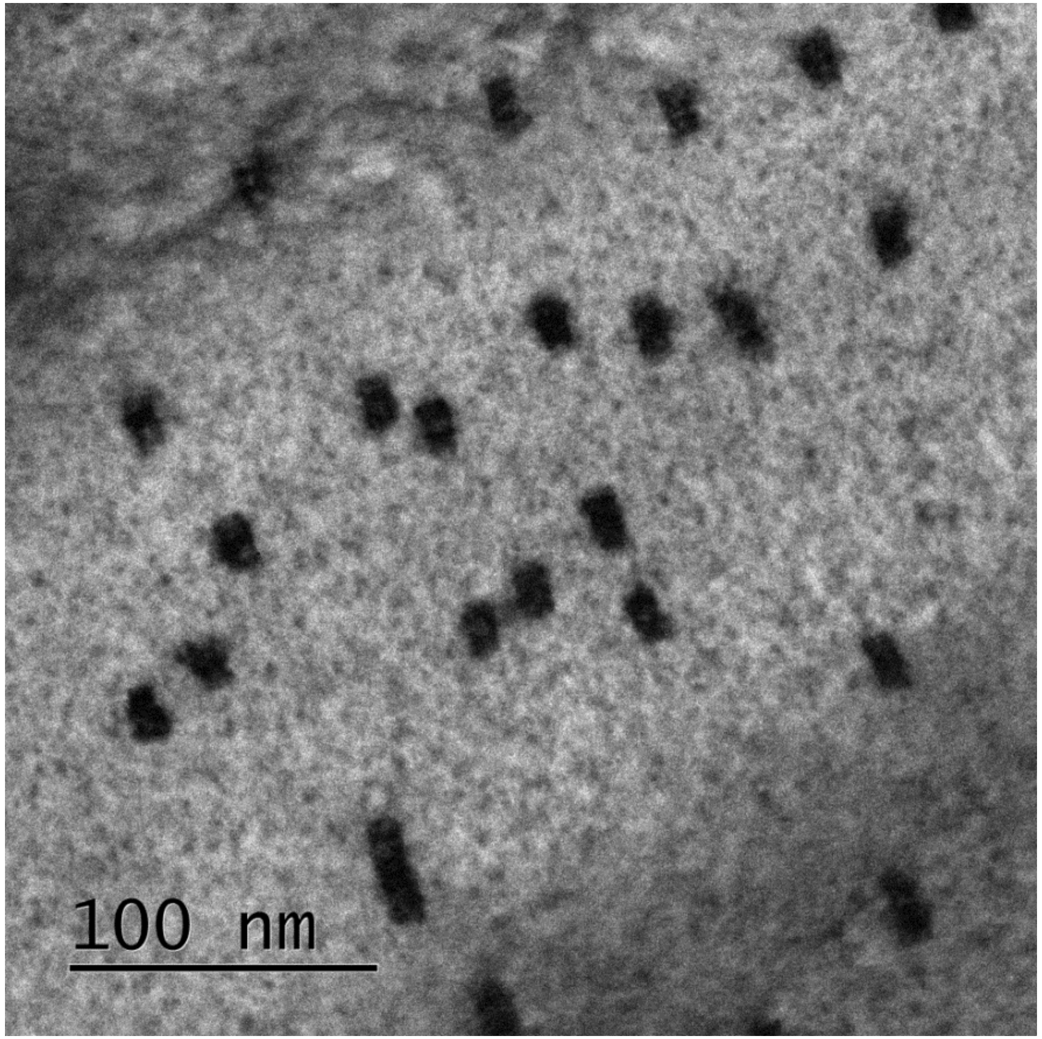
- Lamellae were examined using a double C_s corrected ARM 200F transmission electron microscope (TEM) operating at 200 kV in both TEM and STEM mode.

- FIB lamellae of irradiated material were also annealed in situ using a DENS Solutions Wildfire heating stage in the temperature range 100-300 °C.

TEM BF images in cross section and planar section

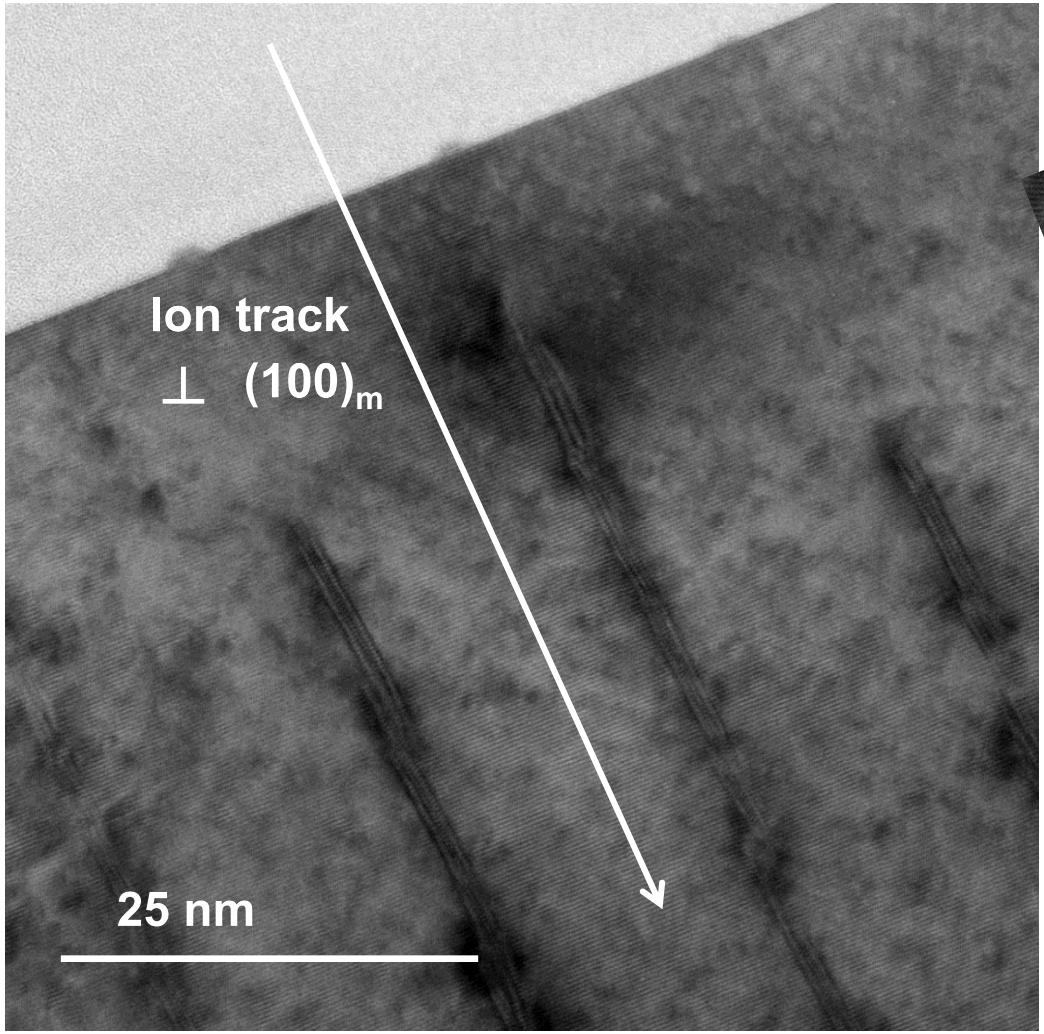


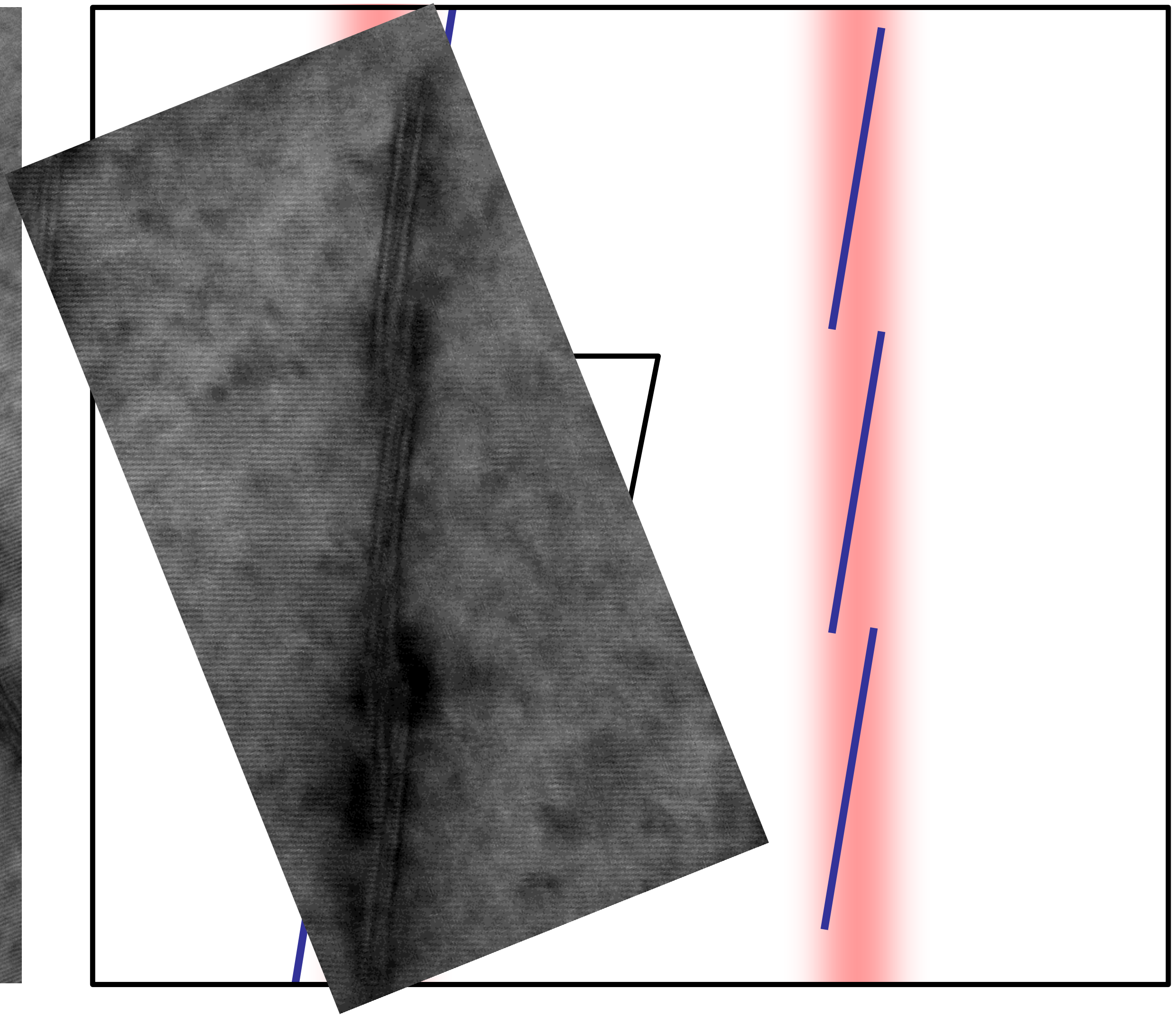
Cross section of segmented t-tracks



Planar section of tracks

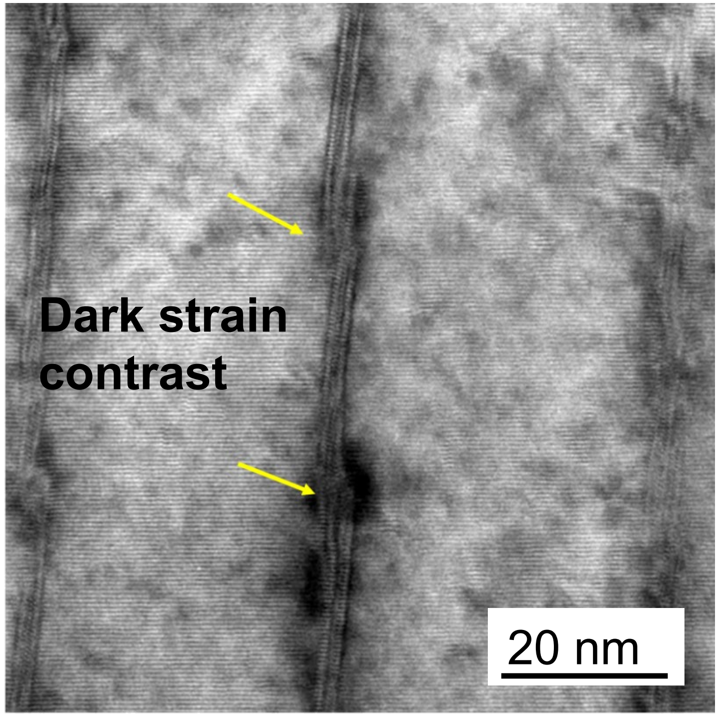
Tetragonal Track Discontinuity





Note: Angle between sections and the continuous line is approximately 9 degrees

t-segments stability - Garvie Equation prediction



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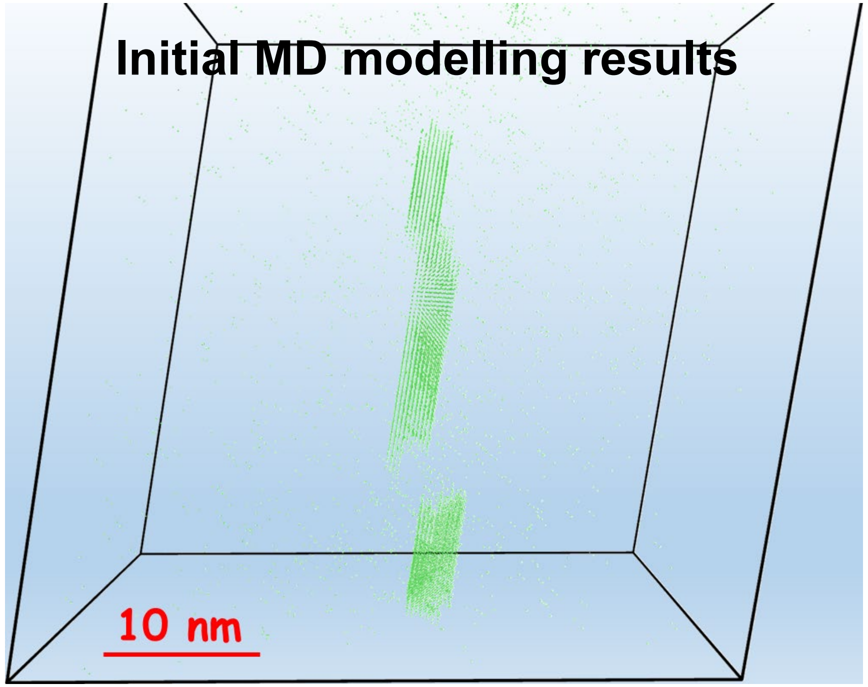
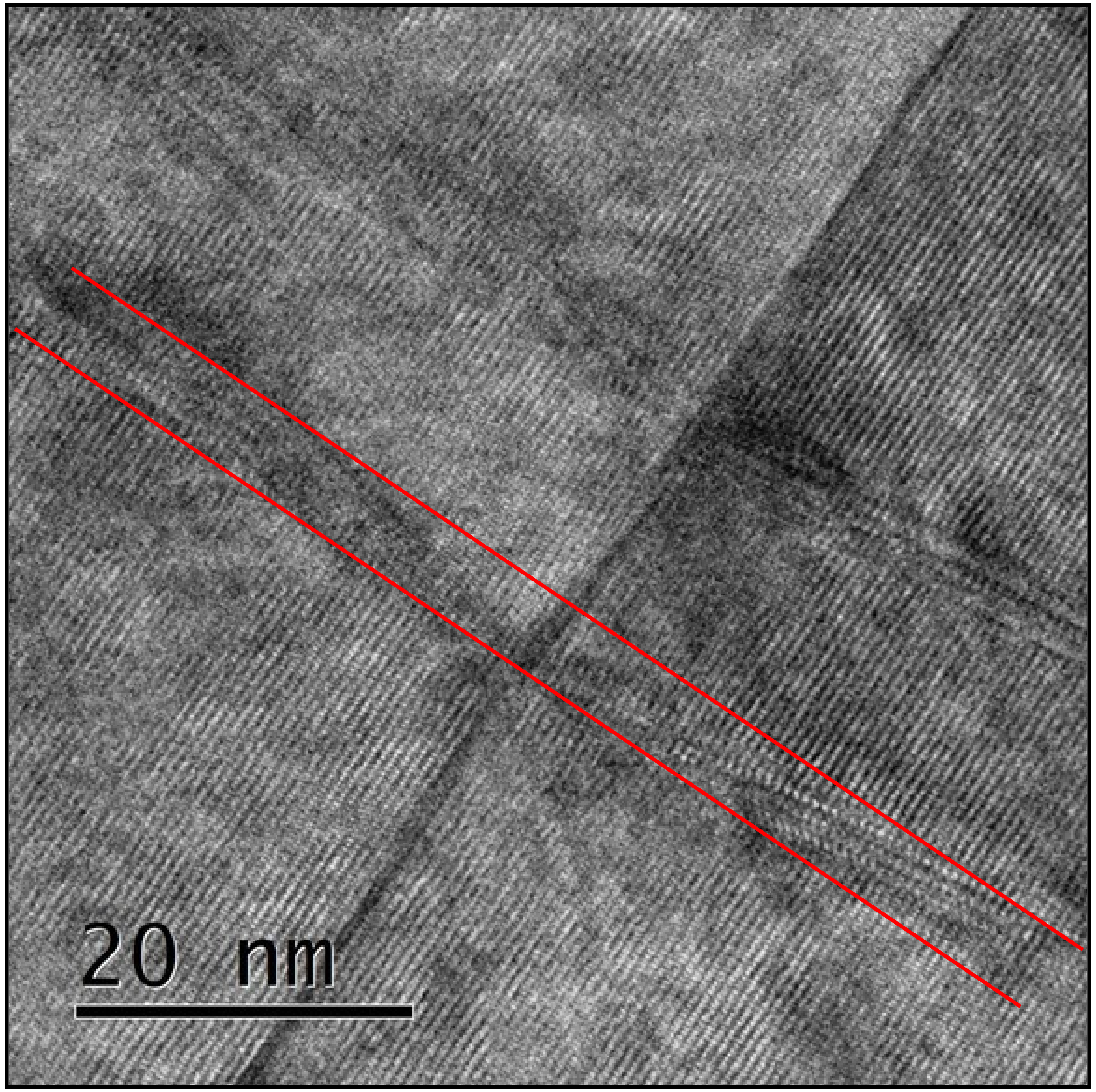


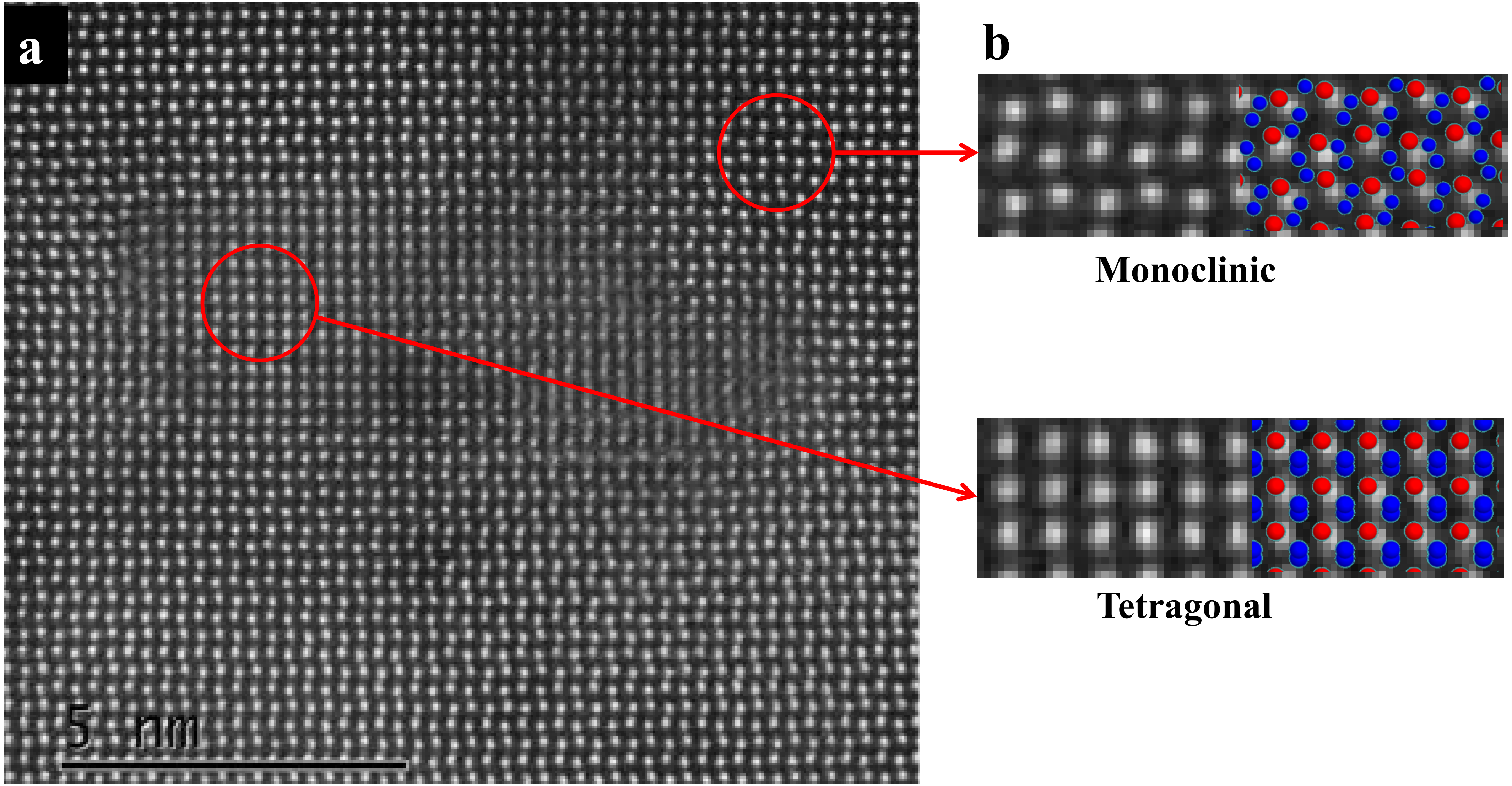
Critical size will depend on the surface energy difference between the tetragonal and monoclinic phases, the free energy difference for an infinite crystal, the change in internal strain energy for embedded particles and the heat of transformation per unit volume.

The calculated critical size for m → t, considering a coherent interface, is <2nm which is not in agreement with the t-segment size of ~2,5 x 2,5 x 25nm

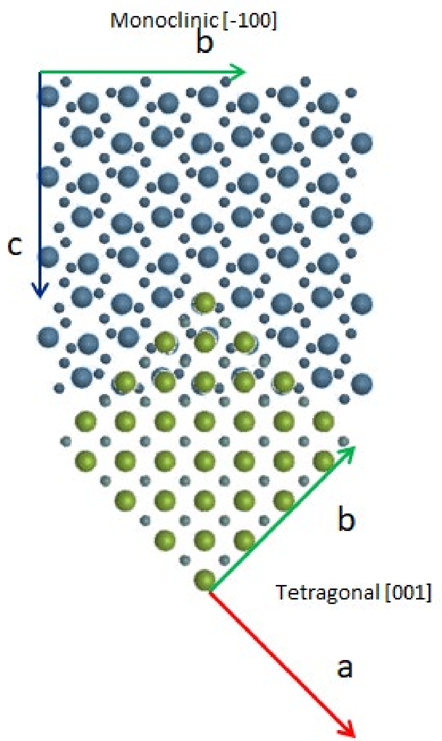
t-track segments across twin boundary in m-zirconia

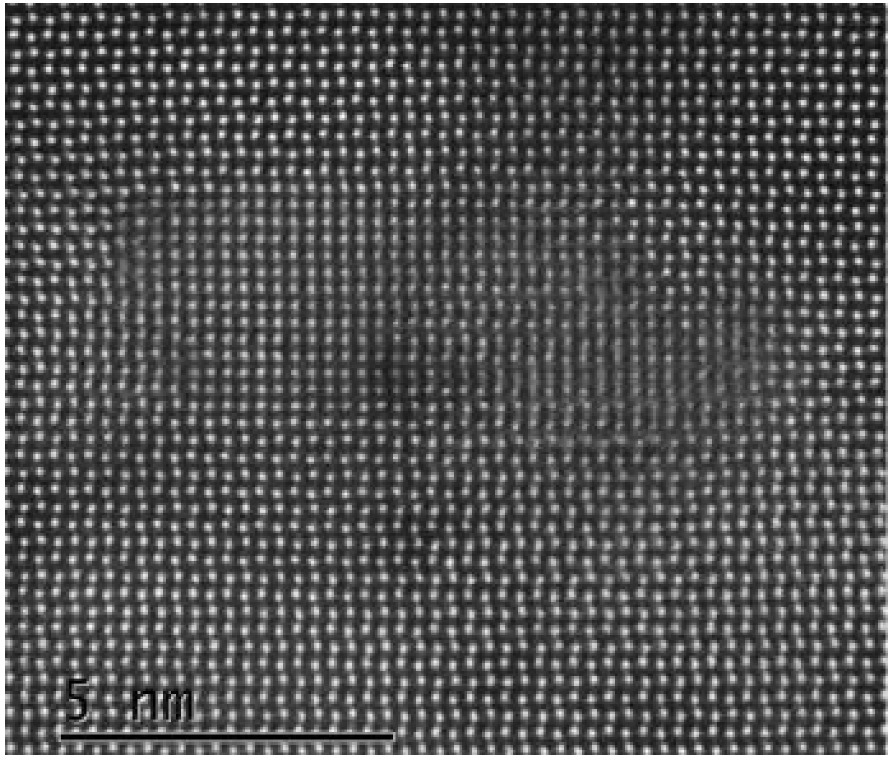


Localized phase transformation – Planar section

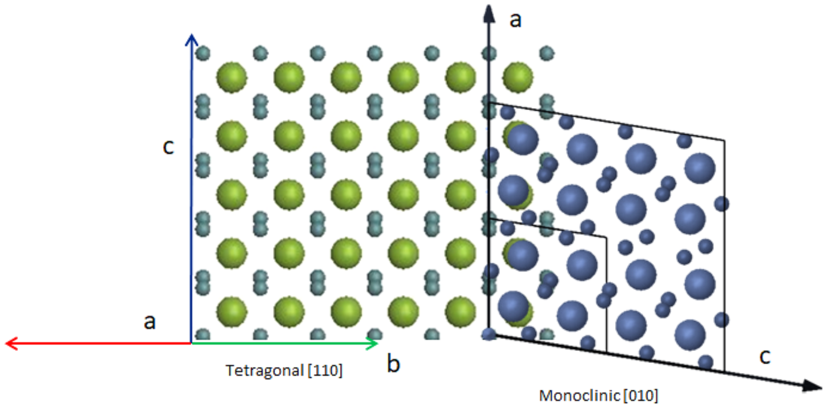


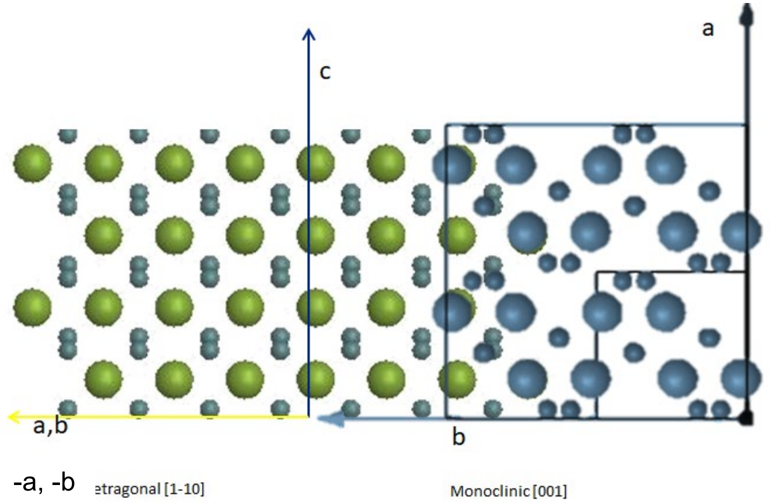
Crystallography – Kelly model





View right to left

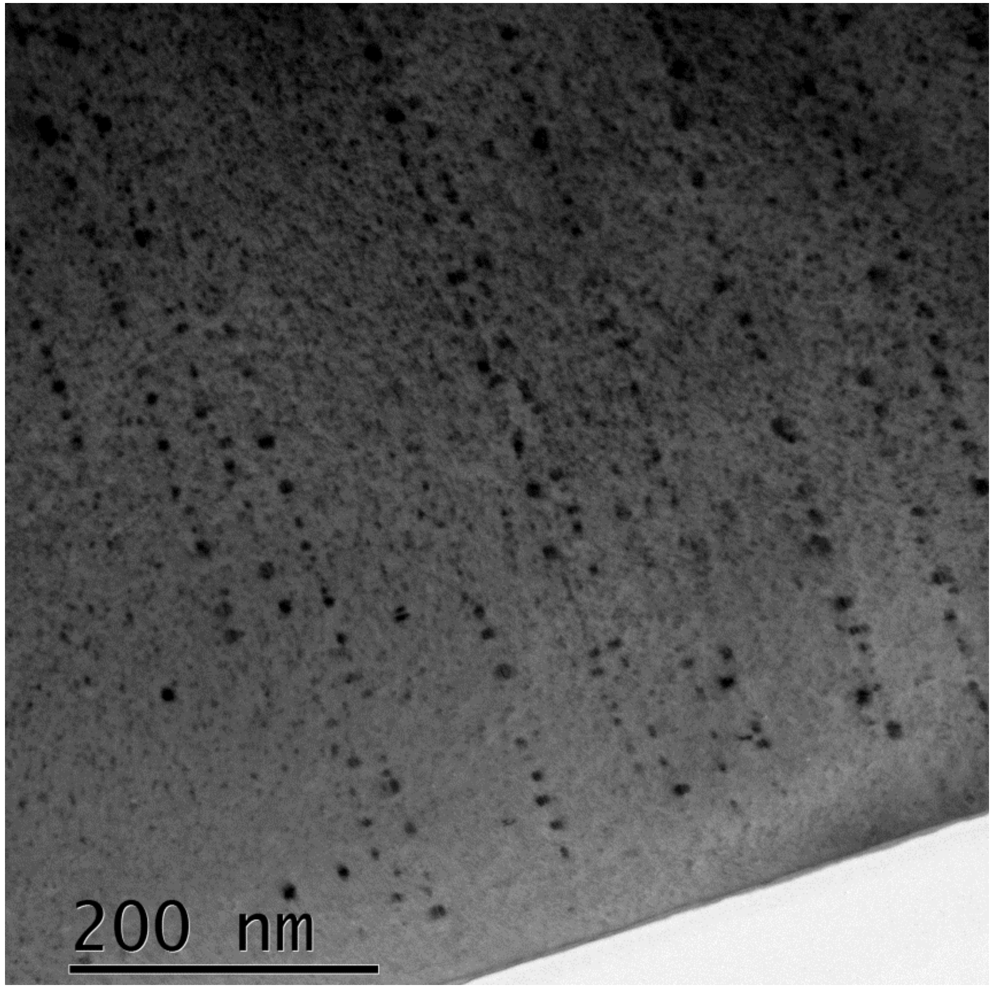


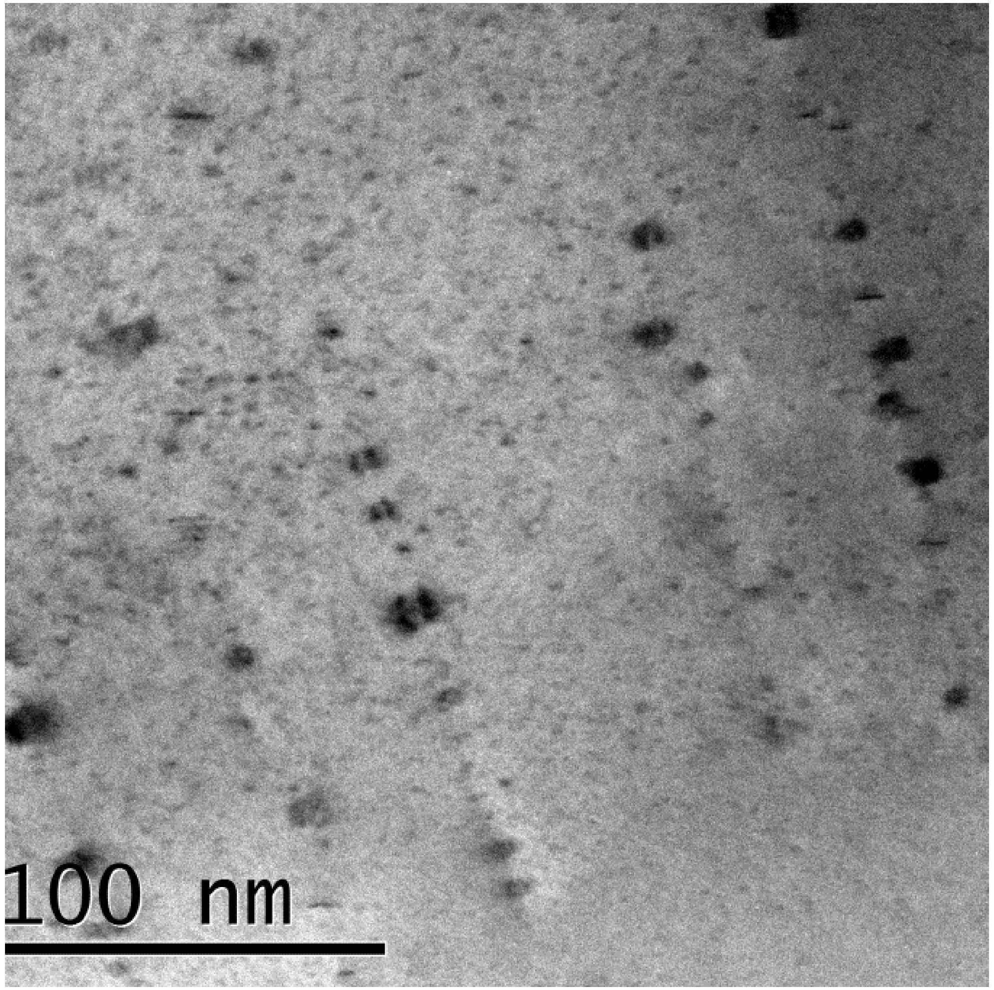


View bottom to top

The crystallographic variant: $(100)_m$ ~|| $((001)_t$, $(001)_m$ ~|| $((010)_t$ and $(010)_m$ ~|| $((100)_t$ is in agreement with the observations made in this study.

TEM BF imaging of in-situ annealing 200-300°C





Conclusions

- We have demonstrated the formation of segmented tetragonal single ion tracks in monoclinic zirconia
- The crystallographic orientation of the t-segment relative to the parent orientation is in agreement with one of the four possible low energy variants proposed by Kelly
- The segment size is not in in agreement with the critical size for stabilization as proposed by the Garvie equation
- Defect loops are formed on annealing in the temperature range 200-300 C. The location of the loops correspond to the position of the junctions (high strain) between segments
- Proposed that the dominant mechanism for the t → m transformation is the diffusion of oxygen vacancies under thermal annealing and strain gradient towards the junctions with the formation of the defect loops. High strain at the junctions acts as a "sink" for the vacancies.

THANK YOU