Nanoscale characterization of beryllide materials

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The most recent version of the Helium Cooled Pebble Bed (HCPB) foreseen for the European DEMO blanket considers solid blocks of titanium beryllide as neutron multiplicator material. The advantage of beryllide materials over pure beryllium is their higher operating temperature, higher corrosion resistance, lower swelling, and retention of tritium under neutron irradiation. Understanding the micro- and nanostructure especially after neutron irradiation is of crucial importance for the qualification process of the material.

The focus of this work will lie on the transmission electron microscopy (TEM) characterization of a titanium beryllide/beryllium composite material irradiated at two different temperatures during the HIDOBE neutron irradiation campaign. In particular, the structure and chemistry of the nanosized cavities in the pure beryllium region and the beryllide region was analyzed and is compared to each other. Apart from the cavities, structural defects were observed in the beryllide region that are not known from irradiated pure beryllium.

The presented results can be used for understanding and quantifying for example tritium retention in beryllide materials and to further optimize the material synthesis and the breeding blanked design in general.

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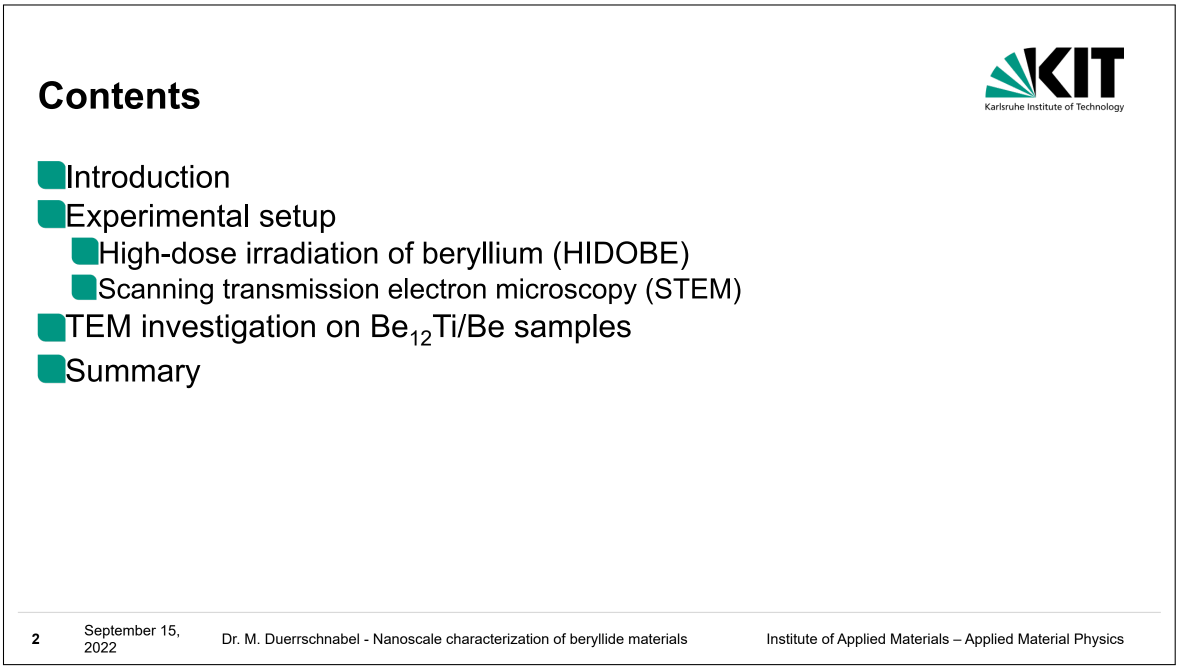

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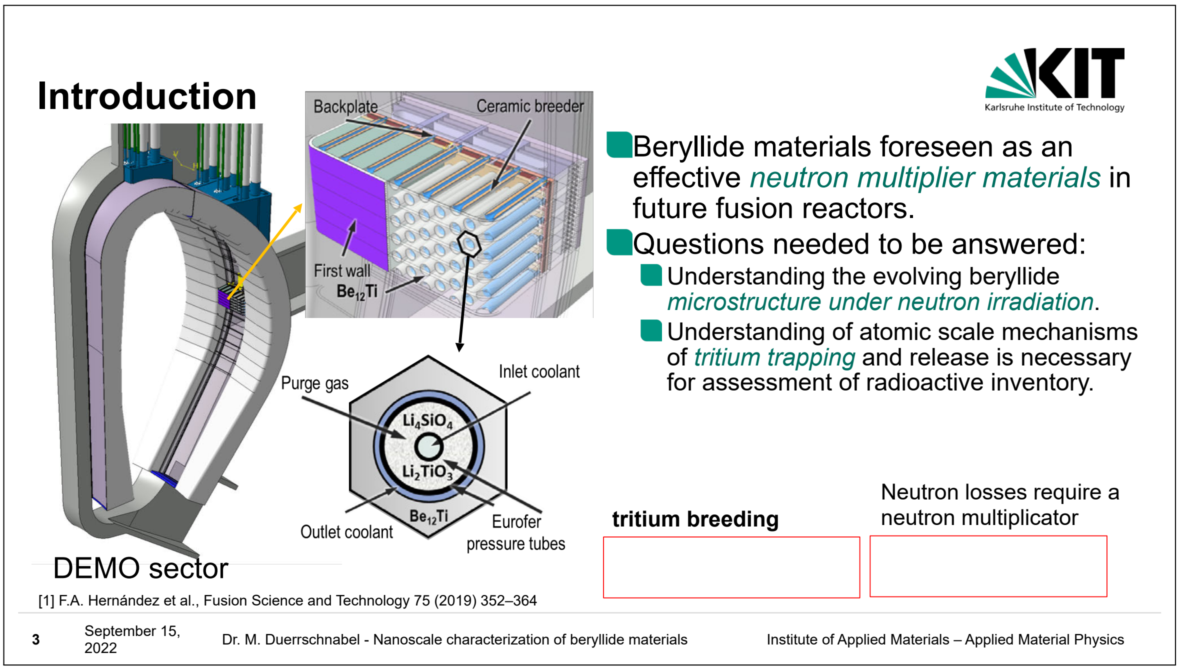


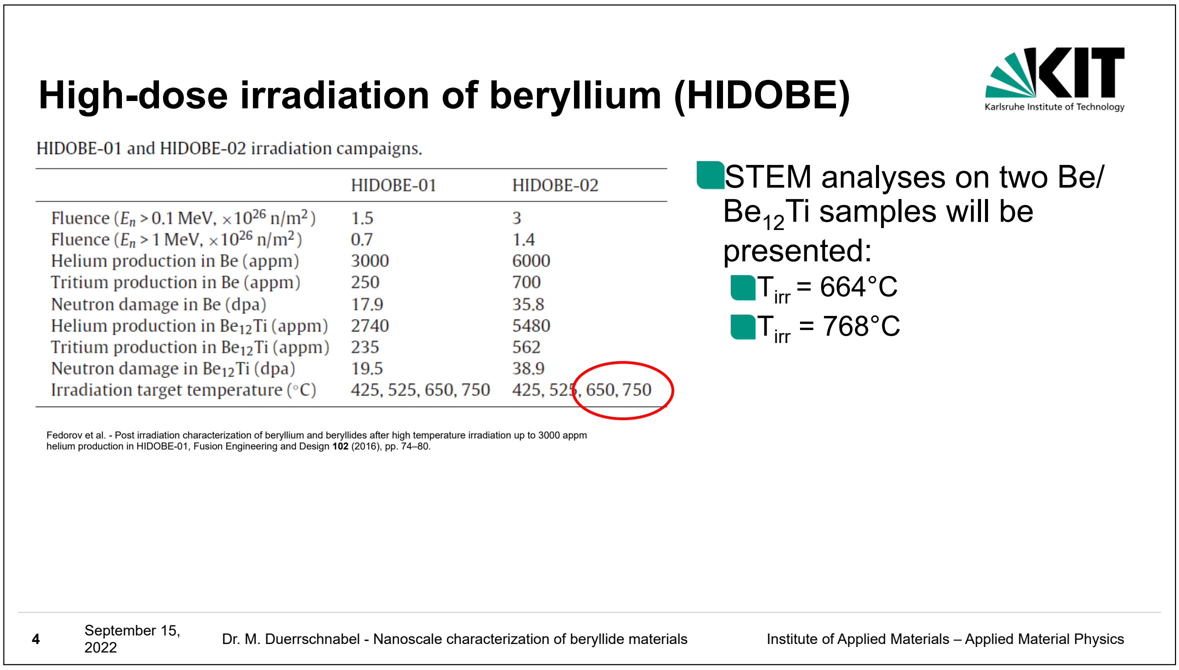
Introduction

[1] F.A. Hernández et al., Fusion Science and Technology 75 (2019) 352–364

- Beryllide materials foreseen as an effective *neutron multiplier materials* in future fusion reactors.
- Questions needed to be answered:
  - Understanding the evolving beryllide *microstructure under neutron irradiation*.
  - Understanding of atomic scale mechanisms of *tritium trapping* and release is necessary for assessment of radioactive inventory.

tritium breeding

Neutron losses require a neutron multiplicator



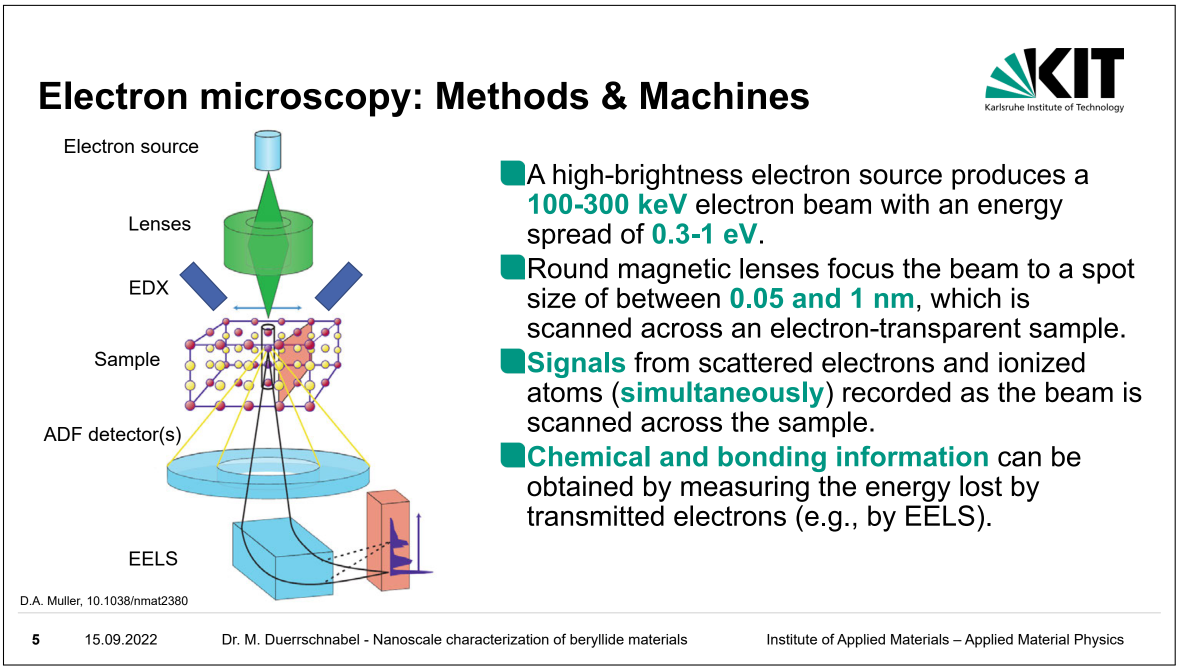
High-dose irradiation of beryllium (HIDOBE)

HIDOBE-01 and HIDOBE-02 irradiation campaigns.

	HIDOBE-01	HIDOBE-02
Fluence ($E_n > 0.1$ MeV, $\times 10^{26}$ n/m^2)	1.5	3
Fluence ($E_n > 1$ MeV, $\times 10^{26}$ n/m^2)	0.7	1.4
Helium production in Be (appm)	3000	6000
Tritium production in Be (appm)	250	700
Neutron damage in Be (dpa)	17.9	35.8
Helium production in $Be_{12}Ti$ (appm)	2740	5480
Tritium production in $Be_{12}Ti$ (appm)	235	562
Neutron damage in $Be_{12}Ti$ (dpa)	19.5	38.9
Irradiation target temperature (°C)	425, 525, 650, 750	425, 525, 650, 750

Fedorov et al. - Post irradiation characterization of beryllium and beryllides after high temperature irradiation up to 3000 appm helium production in HIDOBE-01, Fusion Engineering and Design **102** (2016), pp. 74–80.

- STEM analyses on two Be/ $Be_{12}Ti$ samples will be presented:
  - T_{irr} = 664°C
  - T_{irr} = 768°C

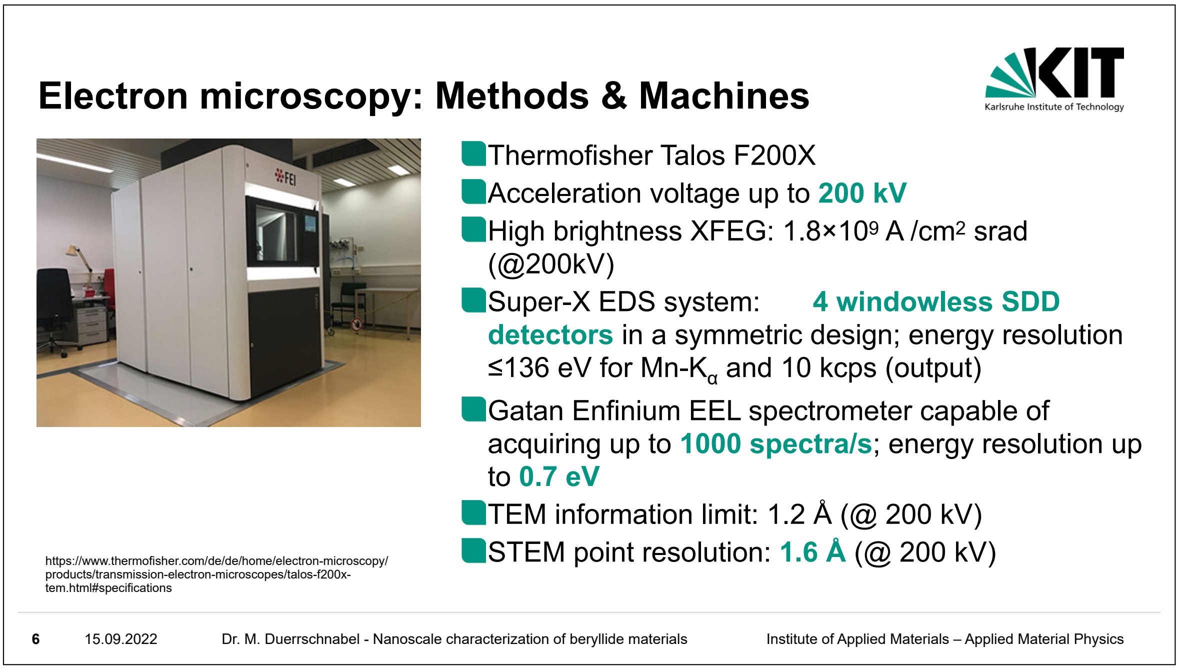


Electron microscopy: Methods & Machines

Karlsruhe Institute of Technology

- A high-brightness electron source produces a **100-300 keV** electron beam with an energy spread of **0.3-1 eV**.
- Round magnetic lenses focus the beam to a spot size of between **0.05 and 1 nm**, which is scanned across an electron-transparent sample.
- **Signals** from scattered electrons and ionized atoms (**simultaneously**) recorded as the beam is scanned across the sample.
- **Chemical and bonding information** can be obtained by measuring the energy lost by transmitted electrons (e.g., by EELS).

D.A. Muller, 10.1038/nmat2380



Electron microscopy: Methods & Machines

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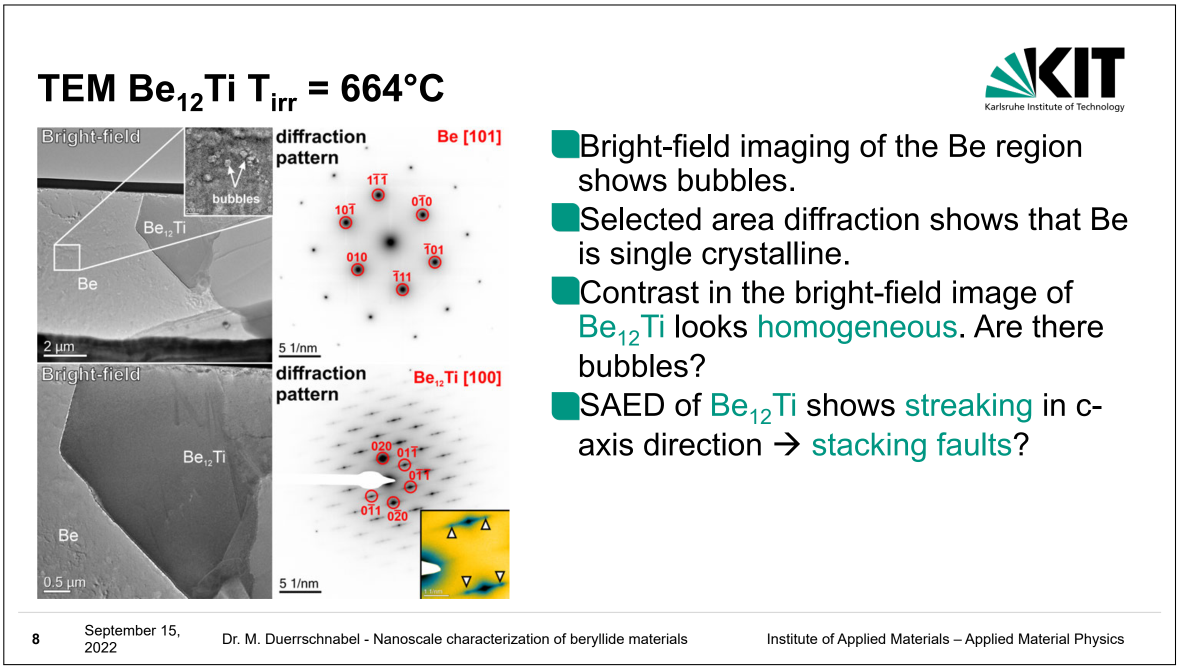
- Thermofisher Talos F200X
- Acceleration voltage up to **200 kV**
- High brightness XFEG: 1.8×10^9 A /cm^2 srad (@200kV)
- Super-X EDS system: **4 windowless SDD detectors** in a symmetric design; energy resolution ≤136 eV for Mn-K_α and 10 kcps (output)
- Gatan Enfinium EEL spectrometer capable of acquiring up to **1000 spectra/s**; energy resolution up to **0.7 eV**
- TEM information limit: 1.2 Å (@ 200 kV)
- STEM point resolution: **1.6 Å** (@ 200 kV)

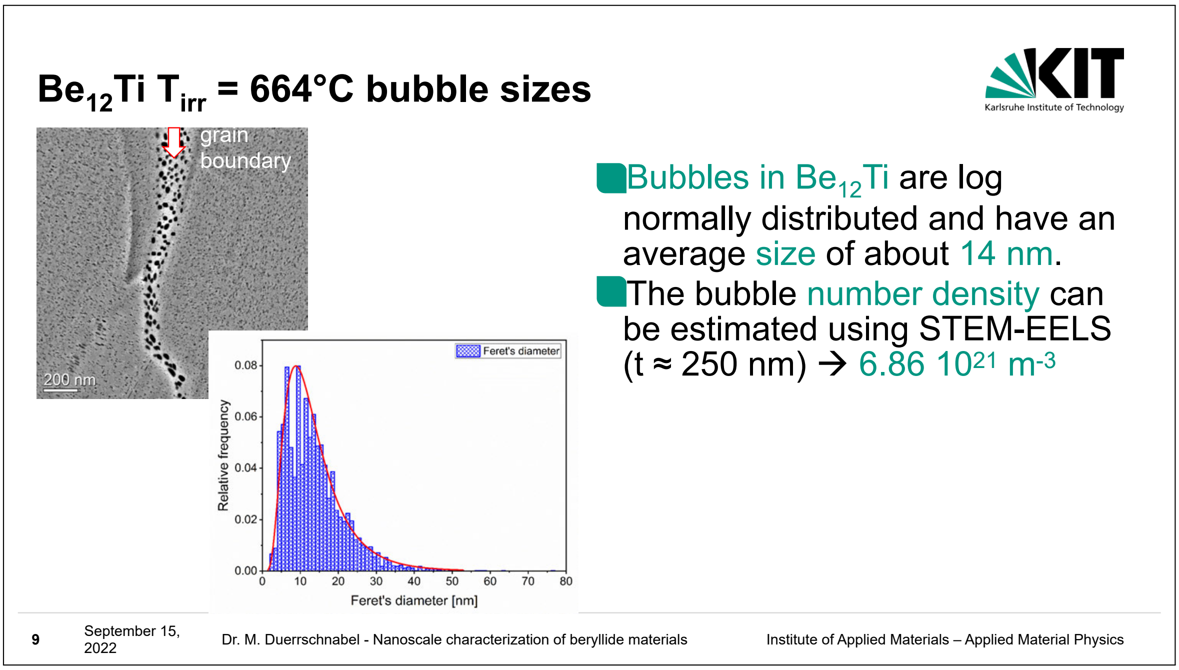
https://www.thermofisher.com/de/de/home/electron-microscopy/products/transmission-electron-microscopes/talos-f200x-tem.html#specifications

Results of $Be_{12}Ti$ sample irradiated at 664°C



TEM $Be_{12}Ti$ T_{irr} = 664°C

- Bright-field imaging of the Be region shows bubbles.
- Selected area diffraction shows that Be is single crystalline.
- Contrast in the bright-field image of $Be_{12}Ti$ looks homogeneous. Are there bubbles?
- SAED of $Be_{12}Ti$ shows streaking in c-axis direction → stacking faults?



$Be_{12}Ti$ T_{irr} = 664°C bubble sizes

- Bubbles in $Be_{12}Ti$ are log normally distributed and have an average size of about 14 nm.
- The bubble number density can be estimated using STEM-EELS (t ≈ 250 nm) → 6.86 10^{21} m^{-3}

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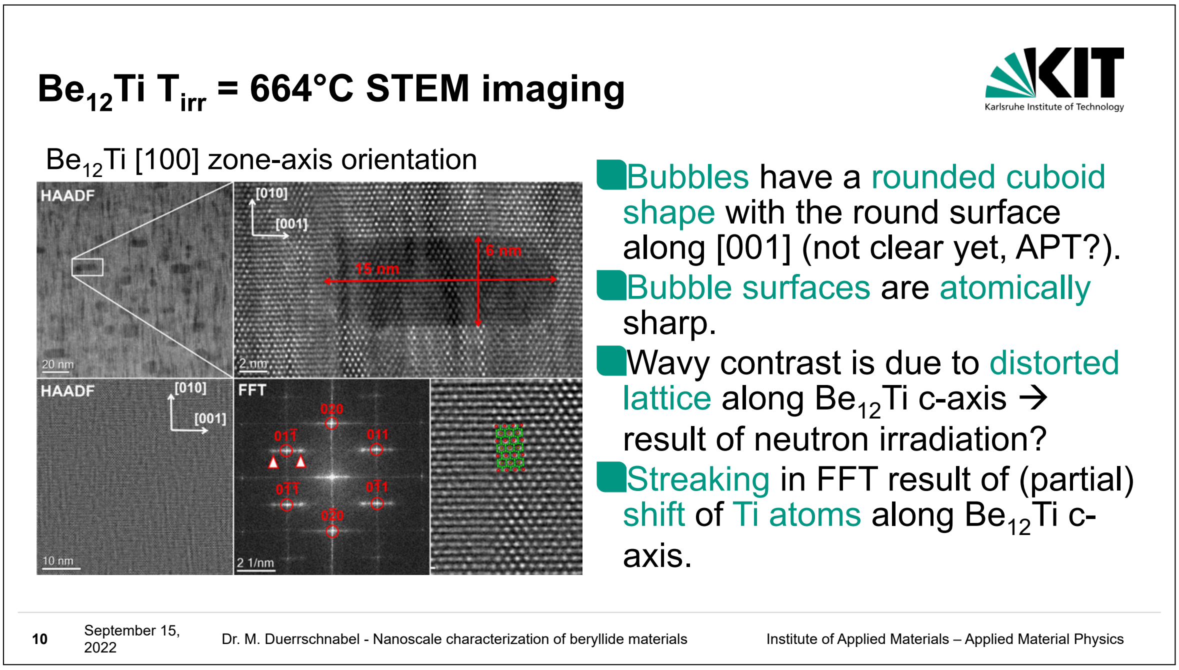

$Be_{12}Ti$ T_{irr} = 664°C STEM imaging

$Be_{12}Ti$ [100] zone-axis orientation

- Bubbles have a rounded cuboid shape with the round surface along [001] (not clear yet, APT?).
- Bubble surfaces are atomically sharp.
- Wavy contrast is due to distorted lattice along $Be_{12}Ti$ c-axis → result of neutron irradiation?
- Streaking in FFT result of (partial) shift of Ti atoms along $Be_{12}Ti$ c-axis.

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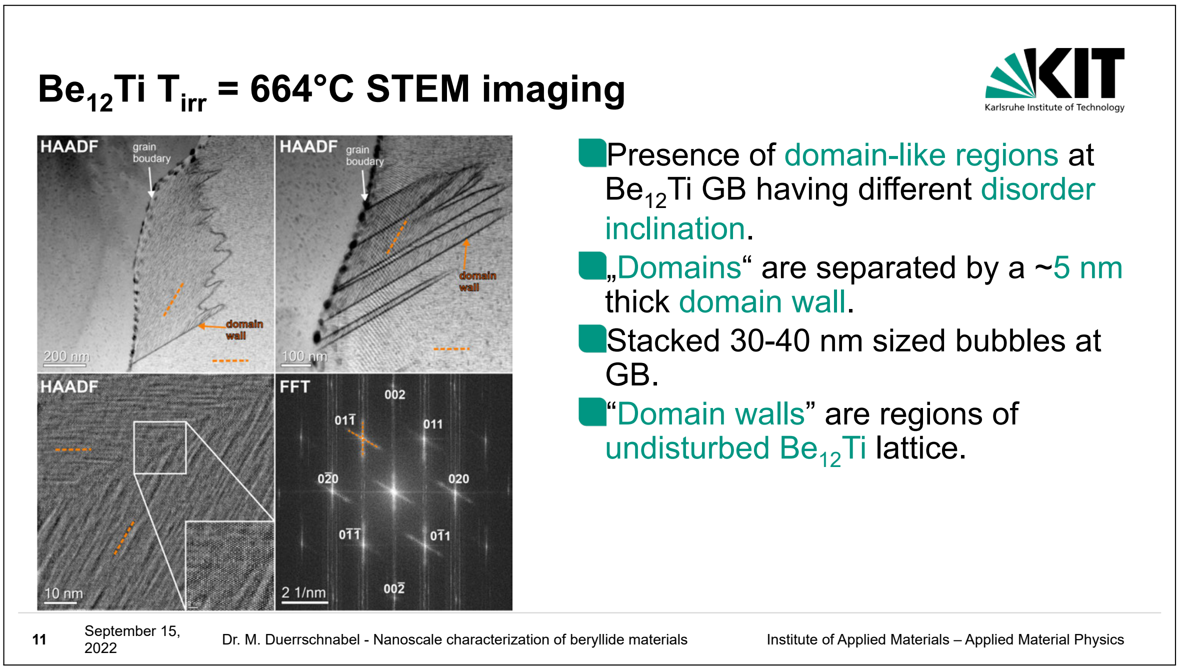
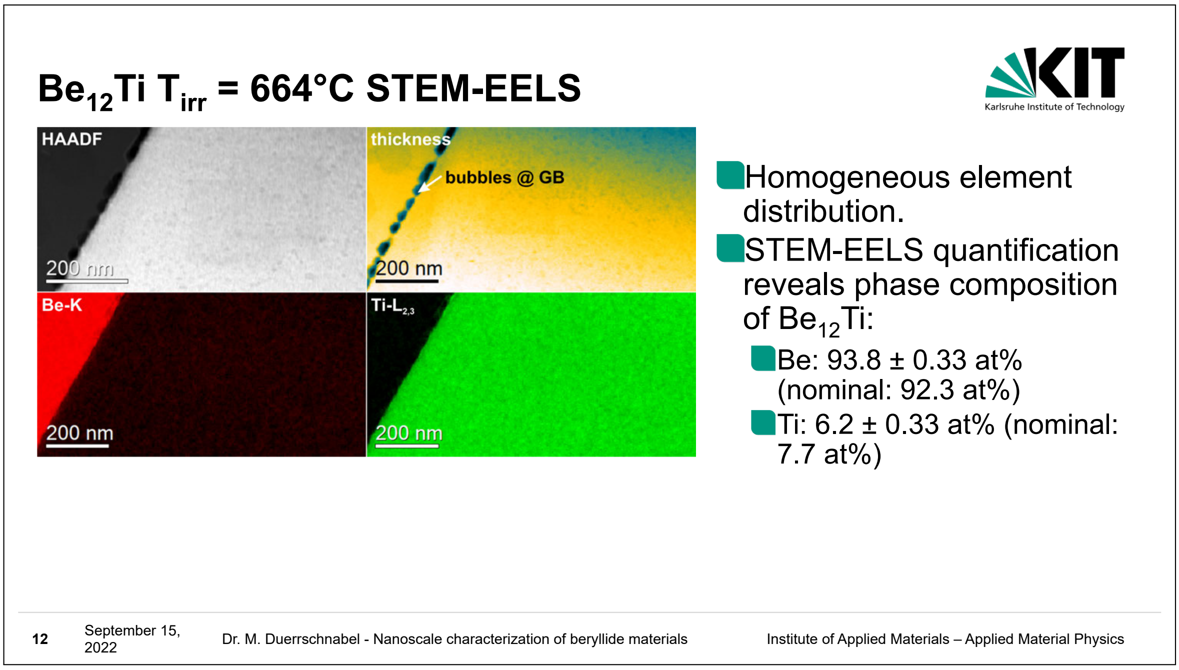


$Be_{12}Ti$ T_{irr} = 664°C STEM imaging

- Presence of domain-like regions at $Be_{12}Ti$ GB having different disorder inclination.
- „Domains“ are separated by a ~5 nm thick domain wall.
- Stacked 30-40 nm sized bubbles at GB.
- “Domain walls” are regions of undisturbed $Be_{12}Ti$ lattice.

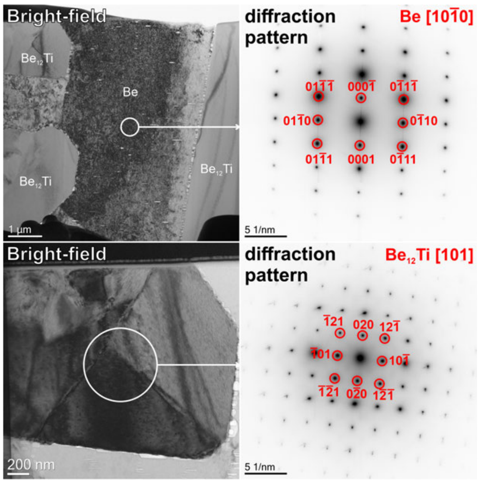


$Be_{12}Ti$ T_{irr} = 664°C STEM-EELS

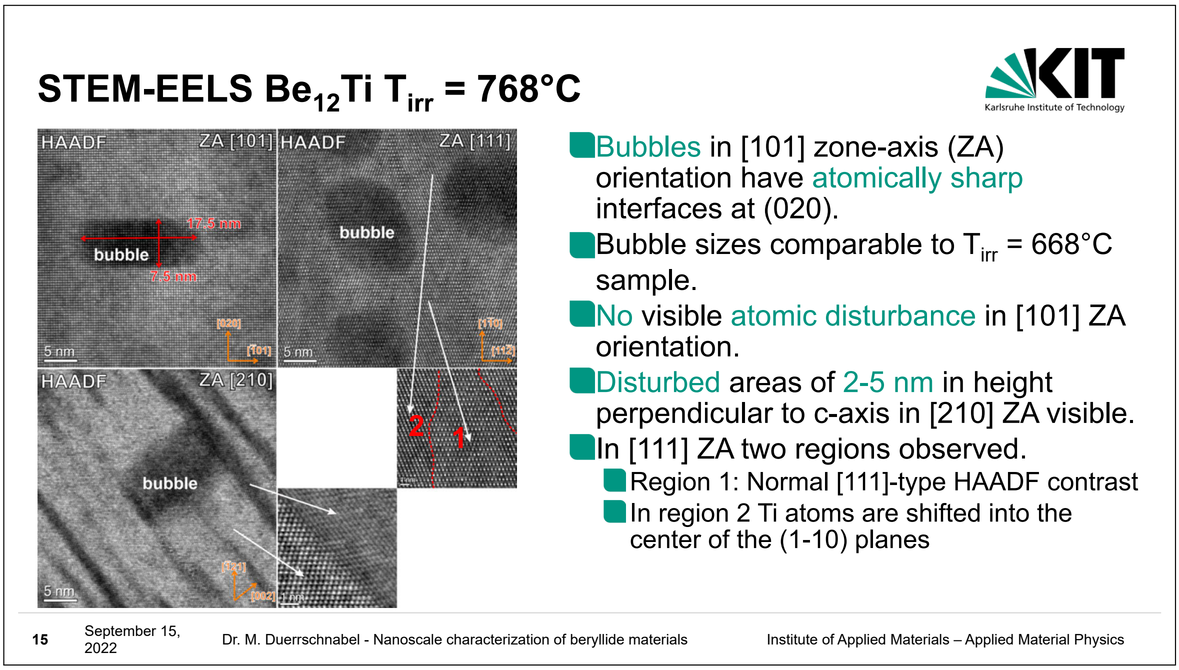
- Homogeneous element distribution.
- STEM-EELS quantification reveals phase composition of $Be_{12}Ti$:
  - Be: 93.8 ± 0.33 at% (nominal: 92.3 at%)
  - Ti: 6.2 ± 0.33 at% (nominal: 7.7 at%)

Results of $Be_{12}Ti$ sample irradiated at 768°C

TEM $Be_{12}Ti$ T_{irr} = 768°C

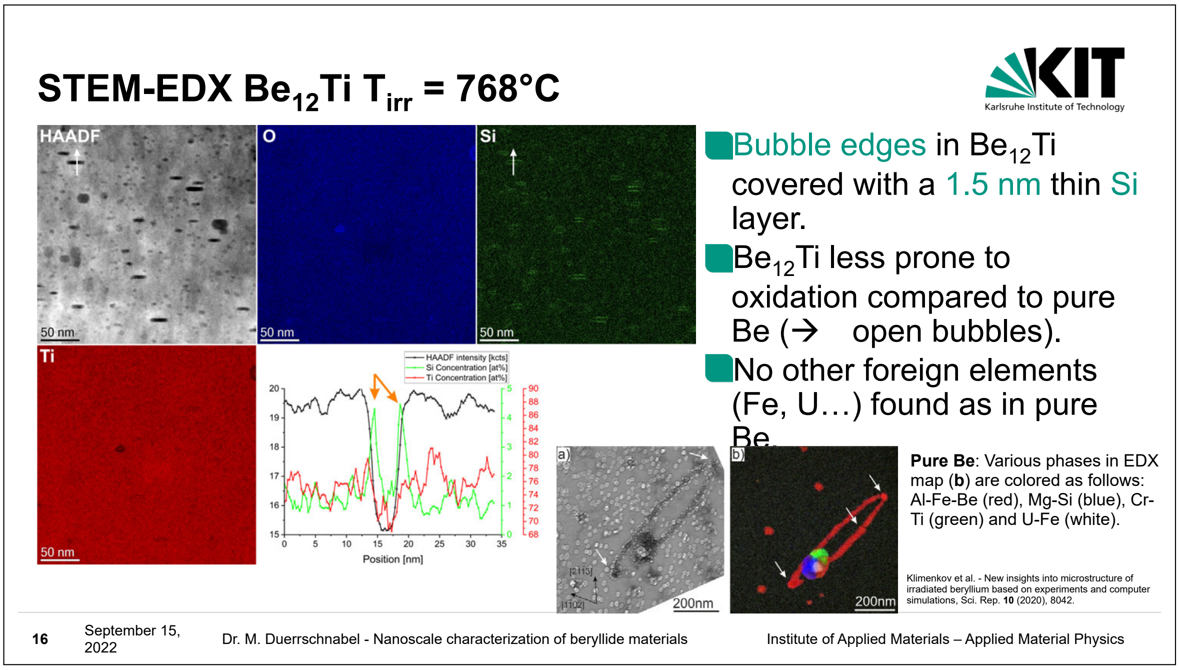


- Be and $Be_{12}Ti$ are both crystalline at T_{irr} = 768°C.
- Be/$Be_{12}Ti$ interfaces are faceted.
- No visible bubbles in $Be_{12}Ti$ at this magnification.
- Large bubbles in Be region and at the Be side of the Be/$Be_{12}Ti$ interface.



STEM-EELS $Be_{12}Ti$ T_{irr} = 768°C

- Bubbles in [101] zone-axis (ZA) orientation have atomically sharp interfaces at (020).
- Bubble sizes comparable to T_{irr} = 668°C sample.
- No visible atomic disturbance in [101] ZA orientation.
- Disturbed areas of 2-5 nm in height perpendicular to c-axis in [210] ZA visible.
- In [111] ZA two regions observed.
  - Region 1: Normal [111]-type HAADF contrast
  - In region 2 Ti atoms are shifted into the center of the (1-10) planes

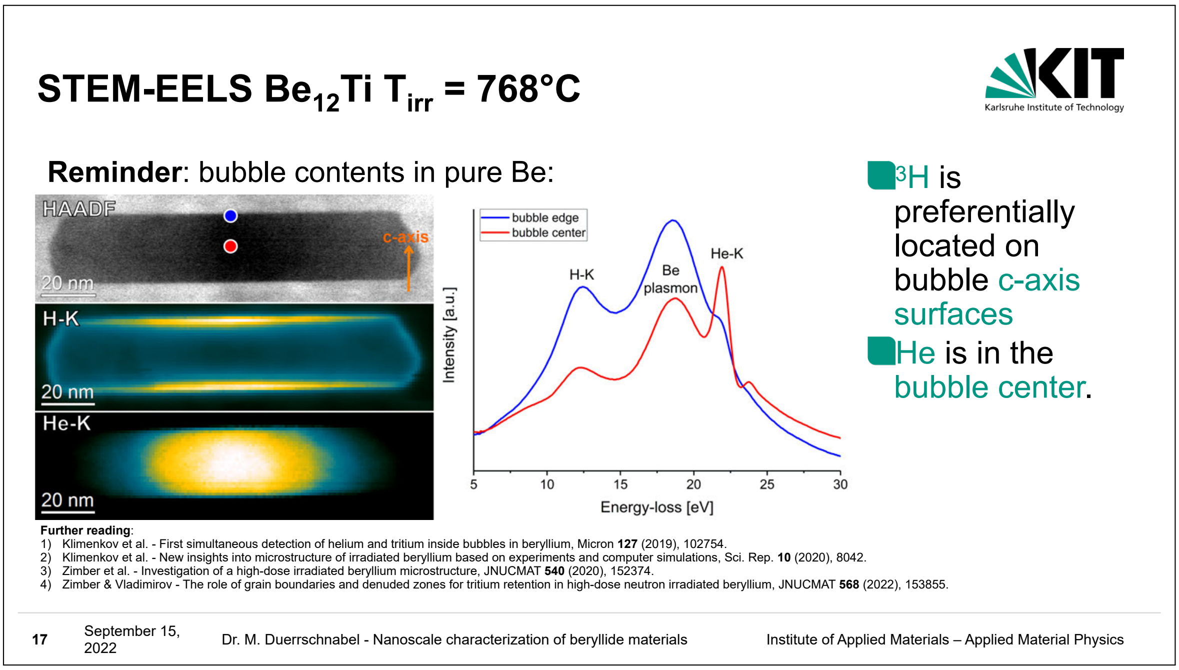


STEM-EDX $Be_{12}Ti$ T_{irr} = 768°C

- Bubble edges in $Be_{12}Ti$ covered with a 1.5 nm thin Si layer.
- $Be_{12}Ti$ less prone to oxidation compared to pure Be (→ open bubbles).
- No other foreign elements (Fe, U…) found as in pure Be.

Pure Be: Various phases in EDX map (**b**) are colored as follows: Al-Fe-Be (red), Mg-Si (blue), Cr-Ti (green) and U-Fe (white).

Klimenkov et al. - New insights into microstructure of irradiated beryllium based on experiments and computer simulations, Sci. Rep. **10** (2020), 8042.



STEM-EELS $Be_{12}Ti$ T_{irr} = 768°C

Reminder: bubble contents in pure Be:

- ^3H is preferentially located on bubble c-axis surfaces
- He is in the bubble center.

Further reading:
1) Klimenkov et al. - First simultaneous detection of helium and tritium inside bubbles in beryllium, Micron **127** (2019), 102754.
2) Klimenkov et al. - New insights into microstructure of irradiated beryllium based on experiments and computer simulations, Sci. Rep. **10** (2020), 8042.
3) Zimber et al. - Investigation of a high-dose irradiated beryllium microstructure, JNUCMAT **540** (2020), 152374.
4) Zimber & Vladimirov - The role of grain boundaries and denuded zones for tritium retention in high-dose neutron irradiated beryllium, JNUCMAT **568** (2022), 153855.

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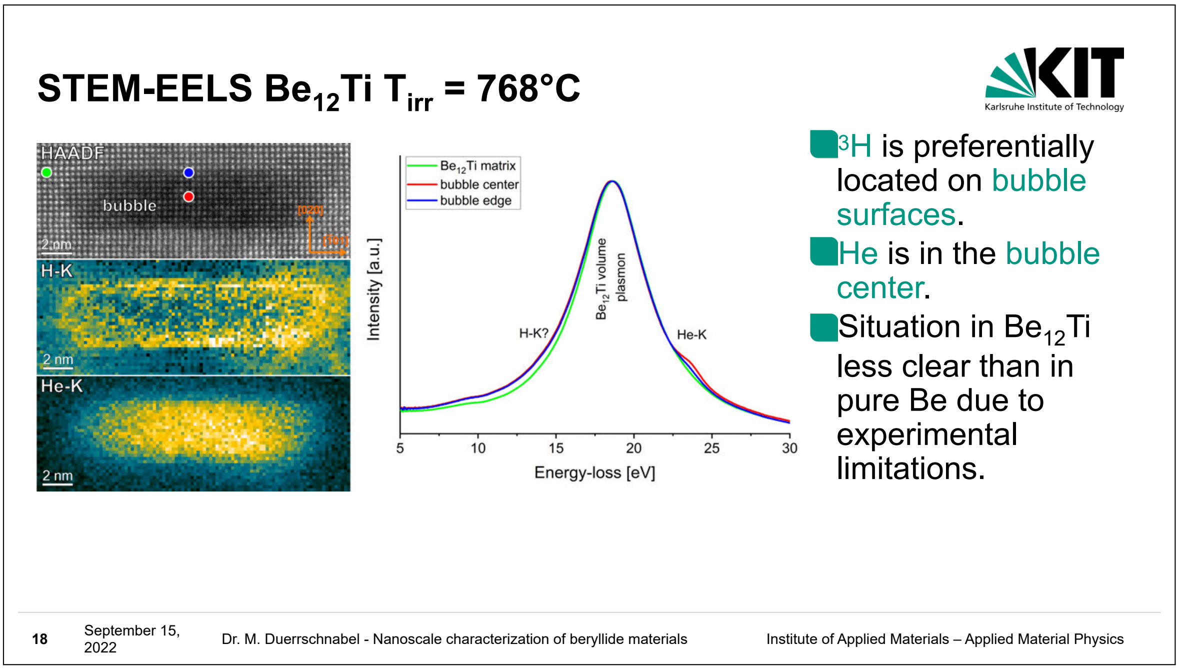

STEM-EELS $Be_{12}Ti$ T_{irr} = 768°C

- ^3H is preferentially located on bubble surfaces.
- He is in the bubble center.
- Situation in $Be_{12}Ti$ less clear than in pure Be due to experimental limitations.

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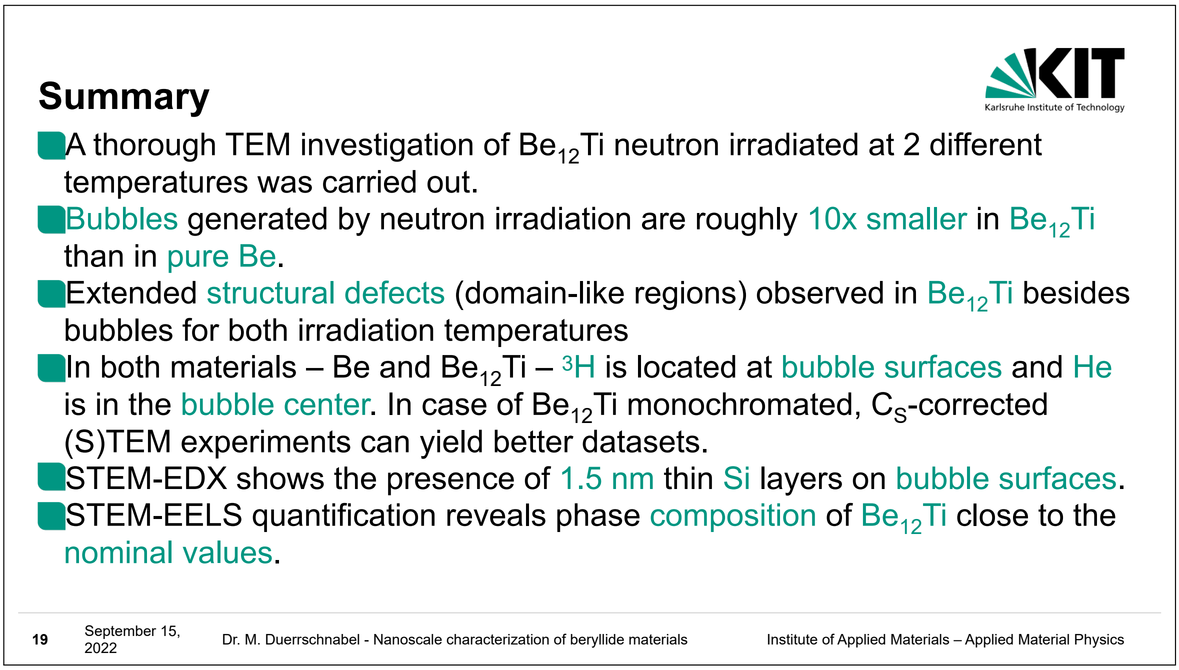

Summary

- A thorough TEM investigation of $Be_{12}Ti$ neutron irradiated at 2 different temperatures was carried out.
- Bubbles generated by neutron irradiation are roughly 10x smaller in $Be_{12}Ti$ than in pure Be.
- Extended structural defects (domain-like regions) observed in $Be_{12}Ti$ besides bubbles for both irradiation temperatures
- In both materials – Be and $Be_{12}Ti$ – ^{3}H is located at bubble surfaces and He is in the bubble center. In case of $Be_{12}Ti$ monochromated, C_S-corrected (S)TEM experiments can yield better datasets.
- STEM-EDX shows the presence of 1.5 nm thin Si layers on bubble surfaces.
- STEM-EELS quantification reveals phase composition of $Be_{12}Ti$ close to the nominal values.

Thank you for your attention!