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Molten Salt Reactor PROGRAM

Beryllium Carbide as Moderator for MSRs

Anne Campbell, ORNL

Oak Ridge National Laboratory | 80

Annual MSR Campaign Review Meeting 16-18 April 2024

Acknowledgements

- D. Sulejmanovic, Y. Osetskiy, E. Zarkadoula, A. Willoughby, E. Cakmak, K. Johnson, B. Henry, E. Paxton, S. Fiscor, J. McFarlane, K. Robb – ORNL
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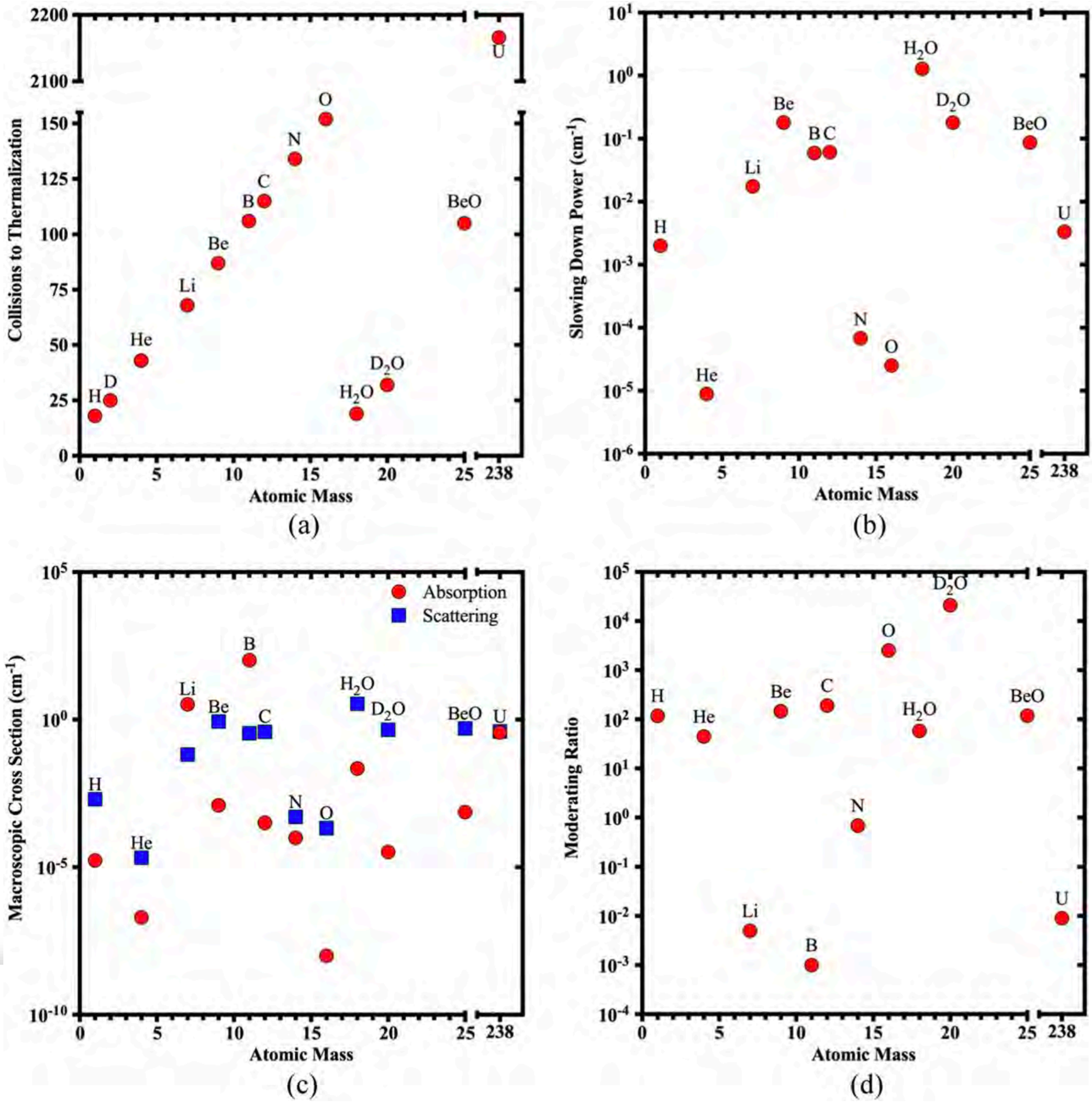
Grand Question

Can beryllium carbide be used in future reactors as a replacement moderator for graphite?

Long-term (10+ years) to answer this question, but can perform preliminary screening

Why Beryllium Carbide?

Campbell & Burchell Timothy D. (2020). Radiation Effects in Graphite. Comprehensive Nuclear Materials 2nd edition, vol. 3, pp. 398–436

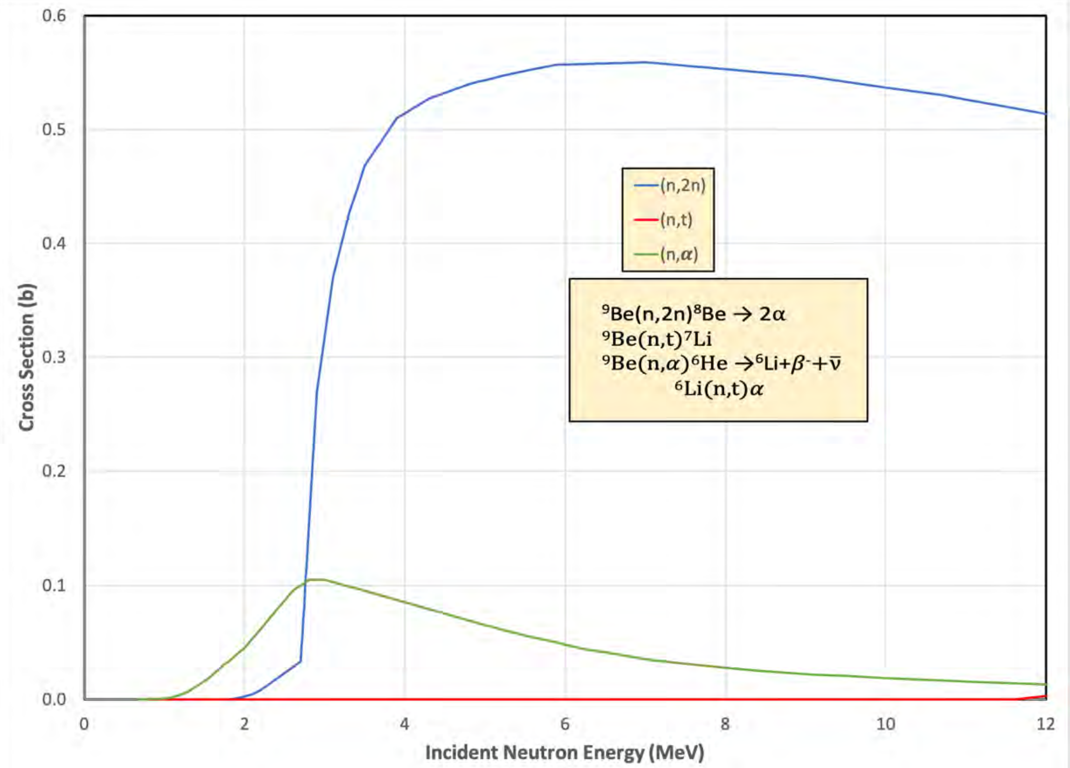


- **High moderating efficiency and low absorption cross section**
- **Be slowing down power ~2.5x > than carbon**
- **Chemically compatible with coolant salts**
- **Antifluorite crystal structure – the same crystalline configuration (with anions and cations reversed) as exceptionally radiation damage resistant fluorite type crystals (e.g., UO_2**
  - The anti-fluorite crystal (Li_2O) has also been shown to have high radiation damage tolerance [1,2]

[1] Moriyama et al., *Journal of Nuclear Materials*, **258-263**, (1998) 587-594.
[2] Noda, et al., *Journal of Nuclear Materials*, **123**, (1984) 908-912

Technical Challenges with Beryllium Carbide

- **Long history of graphite as neutron moderators (CP-1, X-10 ~80 years) research and knowledge – only limited low dose studies in Be_2C [1-3]**
- **Be_2C is brittle, vulnerable to thermal stress cracking**
  - Can we mitigate brittle nature via fiber reinforcement?
- **Be_2C it toxic, moisture sensitive, chemically reacts with U**
  - Would need a protective layer (NbC)
- **Be_2C is a methanide (when exposed to H it decomposes into methane)**
  - Can this be utilized for tritium management strategy?
  - Methane is easily trapped and doesn't diffuse through metal alloys
- **Be does have gas generating reactions with neutrons (He and ^3H)**
  - May be beneficial for fusion systems for ^3H production



Be gas generating reactions (data from ENDF/B-VIII.0)

[1] Maya et al., GA-A-17842; (1985)
[2] Marion & Muenzer, SAND--78-0227C, CONF-780622, (1978)
[3] Feldman & Silverman, NAA-SR-114, (1951)

What are the first steps?

- Need solid Be_2C samples – concern is production and processing is export controlled technology
- Understand high temperature stability of Be_2C
- Preliminary understanding of irradiation effects in Be_2C
- Degradation behavior when exposed to hydrogen
- Understand thermal properties

High Temperature Stability Testing

D. Sulejmanovic

A. Willoughby

E. Cakmak

B. Henry

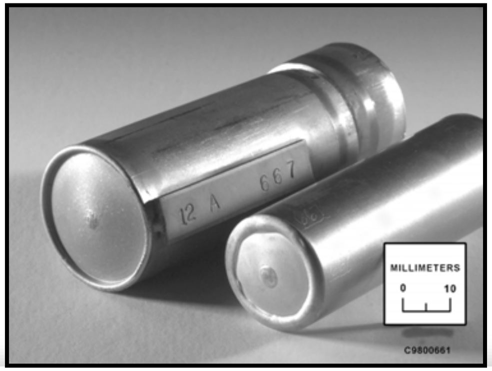
S. Fiscor

Phase Composition Measurement

- **Make Kapton packets, load Be_2C into packet and seal shut with 2 pieces of Kapton tape**
- **Panalytical X'pert diffractometer (CuKα)**
  - θ-2θ setup 20 – 100° 2θ, with a scan rate of 0.0167 deg/s (~30 minute scan time), 1/4° fixed slits, 1/2° anti-scatter slit, 0.04 soller slits coupled with a 10 mm mask, and zero-background plate was positioned below the specimens to remove any peaks from the metal specimen stage
  - Phase identification used a search match with the Jade software and the ICDD database

Static Capsule Testing

- **Mass specimens**
- **Specimens loaded into 316L stainless steel double-containment capsules**
- **Fill with desired environment (Ar gas)**
- **Electron beam welded shut**
- **Put into box furnace at desired temperature for pre-determined time**



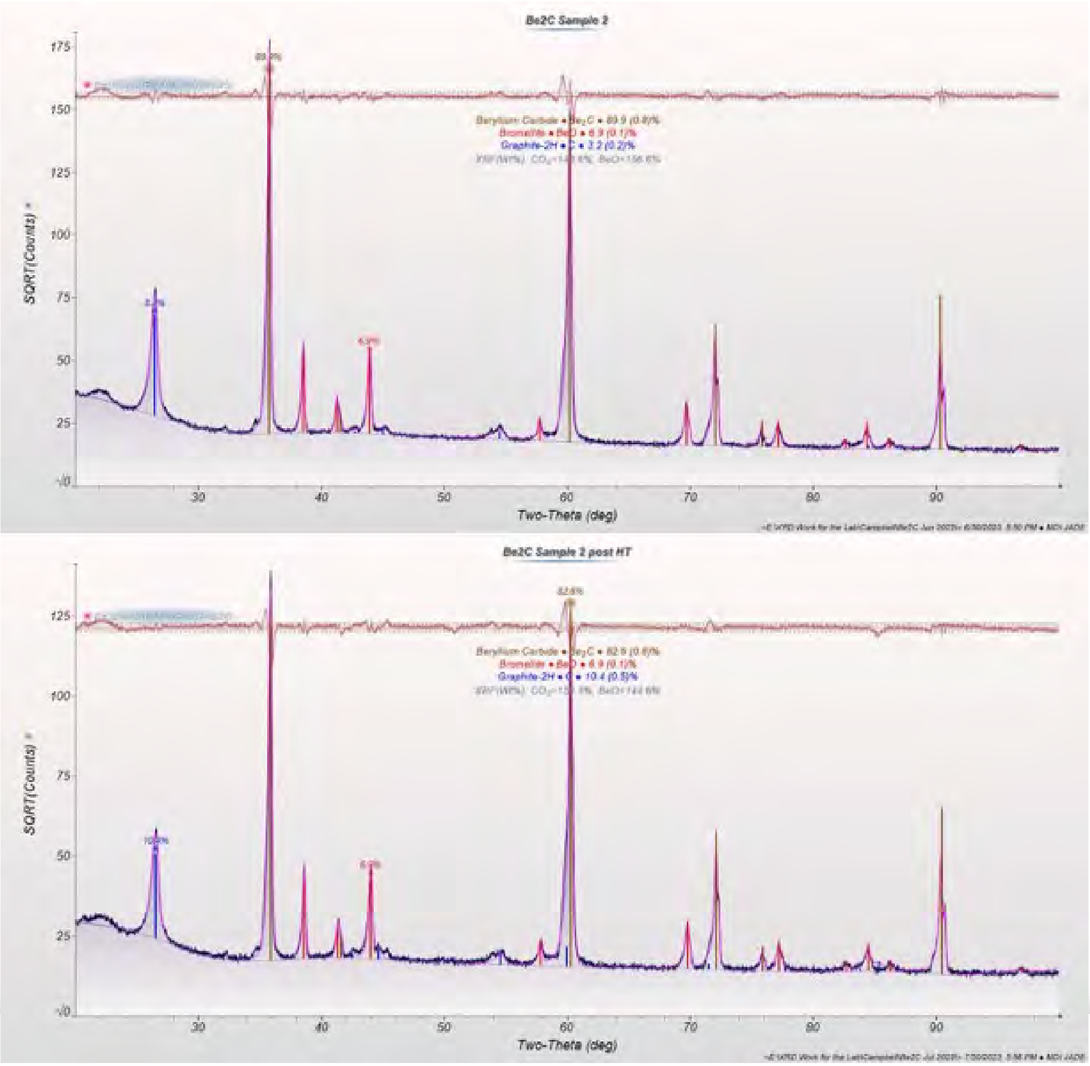
Inner and outer capsules (courtesy J. Keiser)


Before exposure


After exposure

Post-Exposure Analysis

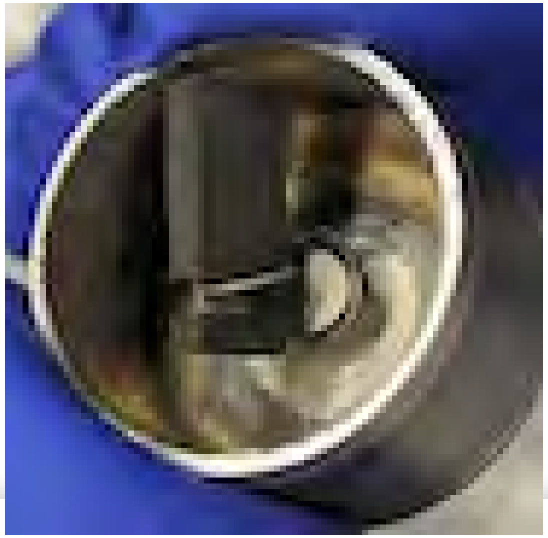
- **Open capsules**
- **Remeasure specimen mass (mass loss)**
- **Package in new Kapton packets**
- **XRD (determine phase composition)**



Summary of Changes 650°C Exposures

Specimen #	Exposure Time	Pre-exposure mass (g)	Post-exposure mass (g)	Mass loss (%)	Be_2C Phase % before / after	BeO Phase % before / after	Graphite Phase % before / after
1	1 day	0.5596	0.5559	0.66	90.2 / 87.2	7.0 / 7.3	2.1 / 5.5
2	1 week	0.6283	0.6234	0.78	89.9 / 82.6	6.9 / 6.9	3.2 / 10.4
3	2 weeks	0.5960	0.5939	0.35	89.6 / 84.4	7.1 / 7.6	3.3 / 8.0

Before exposure



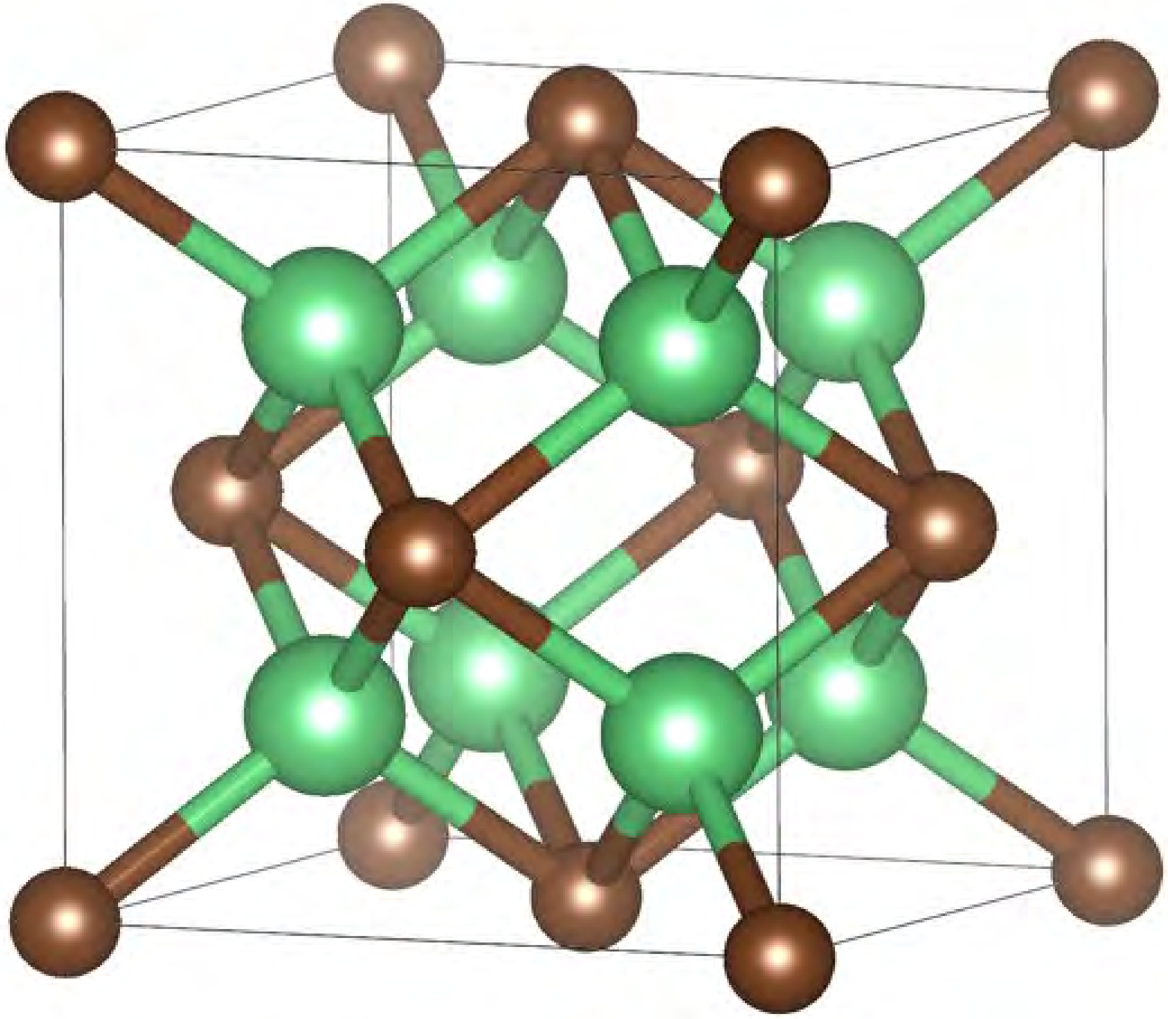
After exposure

Specimens have dull grey finish before exposure.
After exposure, all specimens have dark surface (graphite buildup as Be converts to BeO and sloughs off?)

Modeling Beryllium Carbide

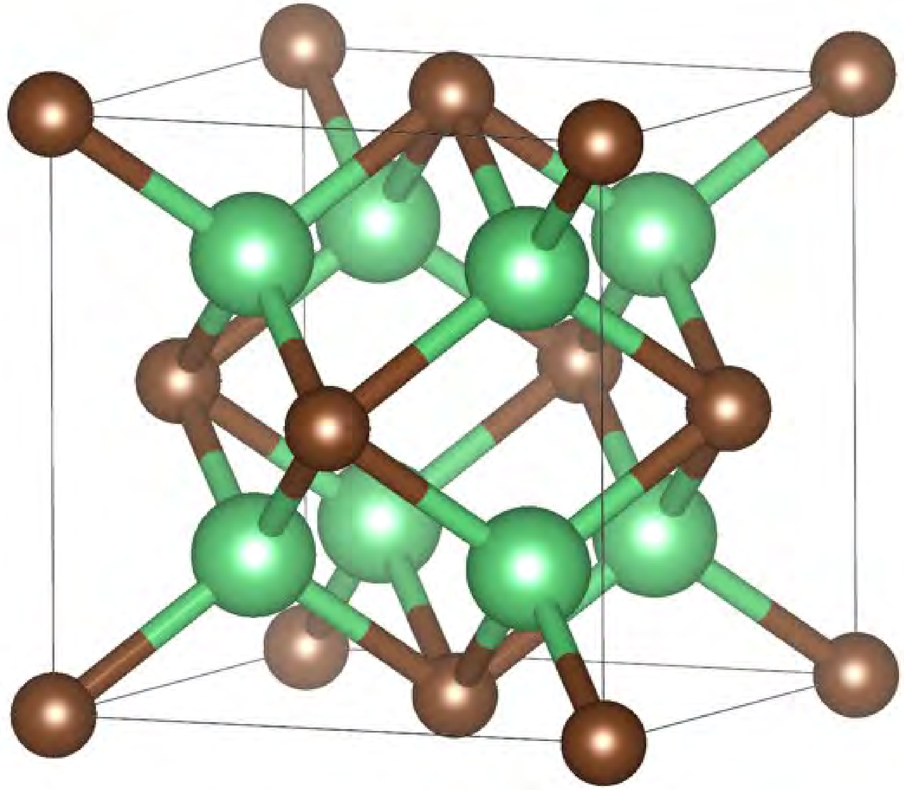
Yuri Osetskiy

Eva Zarkadula



First principles modeling in Be_2C

- **DFT modeling in VASP**
- **Supercells of three sizes were used to investigate different effects: 3x3x3 (324 sites), 4x4x4 (768 sites) and 5x5x5 (1500 sites).**
- **Advanced computing facilities: National Energy Research Scientific Computing Center (NERSC) at LBNL and Compute and Data Environment for Science (CADES) at ORNL.**



Atomic structure of anti-fluorite Be_2C structure: Be – green, C – brown

Band structure

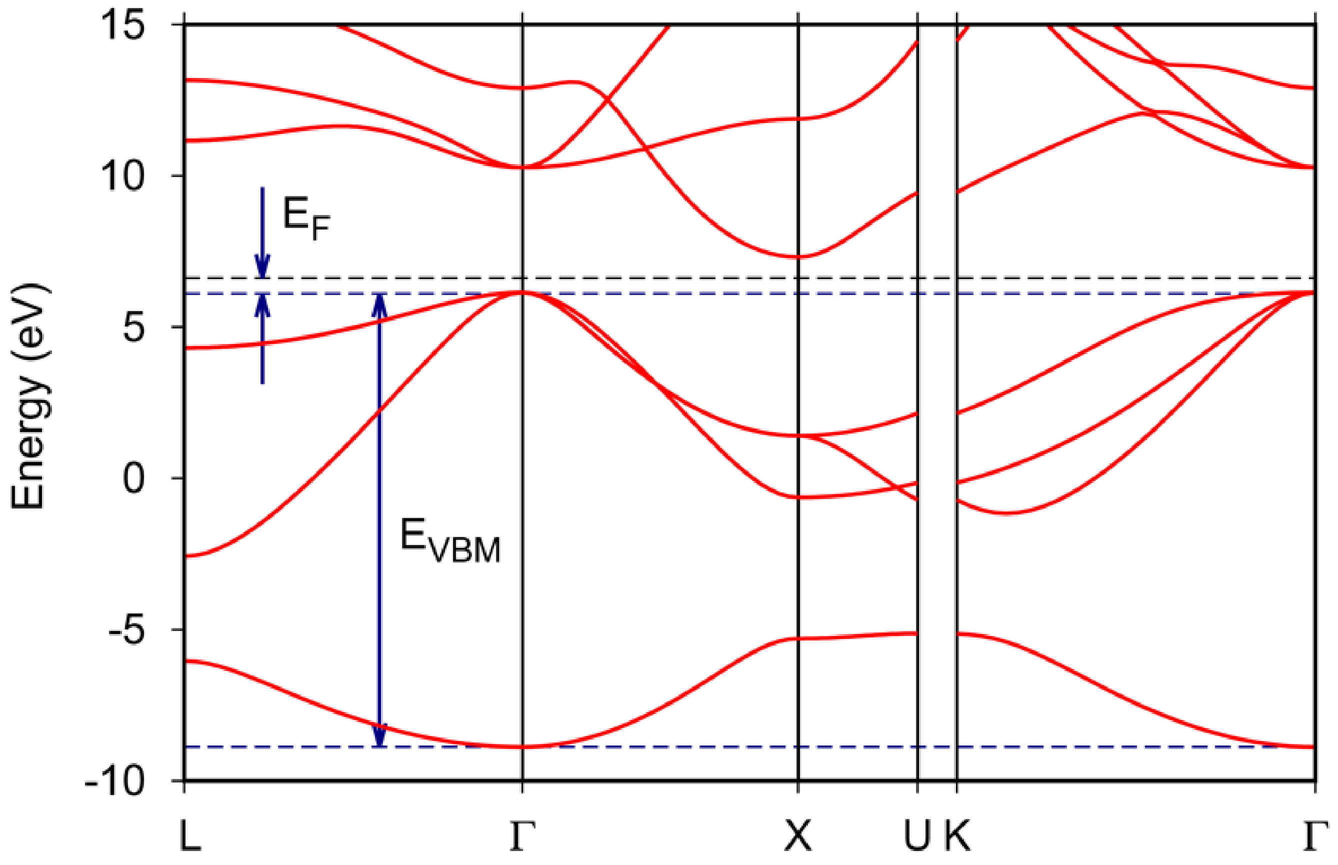
- **Be_2C is weak semiconductor with relatively narrow band gap:**

  $$E_g = 1.212 \text{ eV}$$

- **Estimated Fermi energy:**

  $$E_{Fermi} = 6.271 \text{ eV}$$

Density of states in the perfect Be_2C crystal. E_F is Fermi energy estimated from the valence band maximum – E_{VBM}.



Density of states and point defects

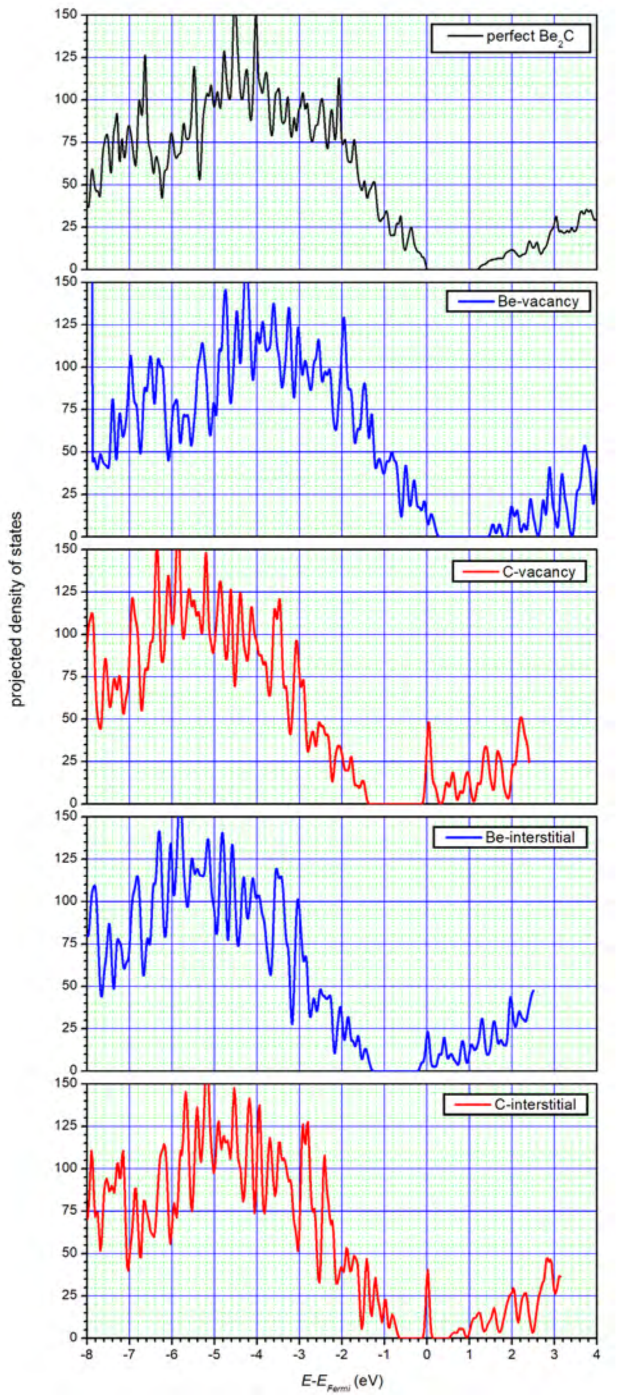
- Be_2C is weak semiconductor with relatively narrow band gap:

  E_g = 1.212 eV

- Estimated Fermi energy:

  E_{Fermi} = 6.271 eV

- Defects change electronic structure by shifting energy and introducing new electronic states.

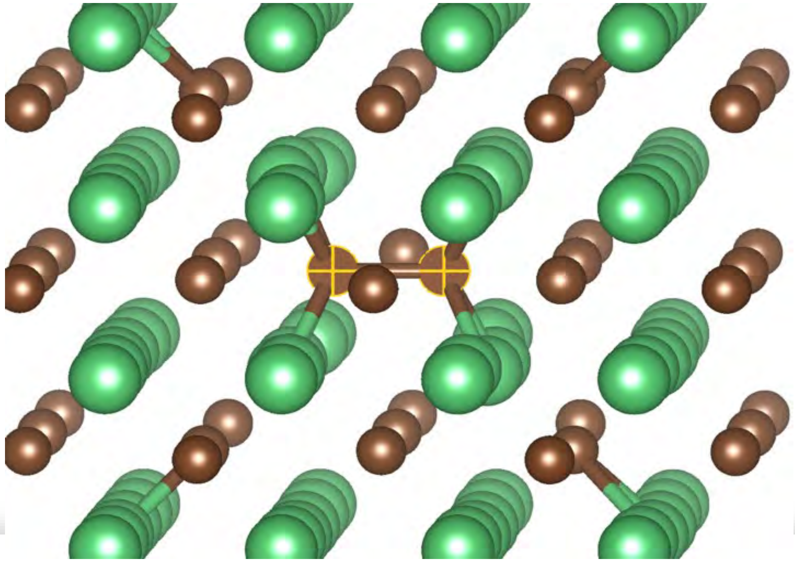


Projected density of states in Be_2C crystals top to bottom: perfect, and containing neutral Be-vacancy, C-vacancy, Be-interstitial and C-interstitial.

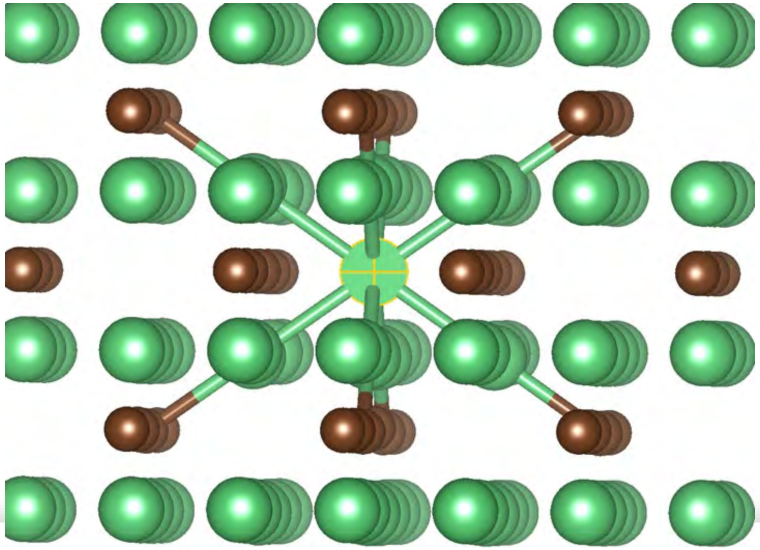
Point defects properties interstitial structures

Ground state configurations:

- **Anti-fluorite Be_2C structure assumes many possible configurations of interstitial atoms**
- **For estimating the ground state configuration, we applied DFT molecular dynamics modeling – annealing over 4 ps at 1200K followed by relaxation to 0K**



Symmetric split C-C dumbbell along [100] direction;



Octahedral Be-interstitial between the Be (001) planes.

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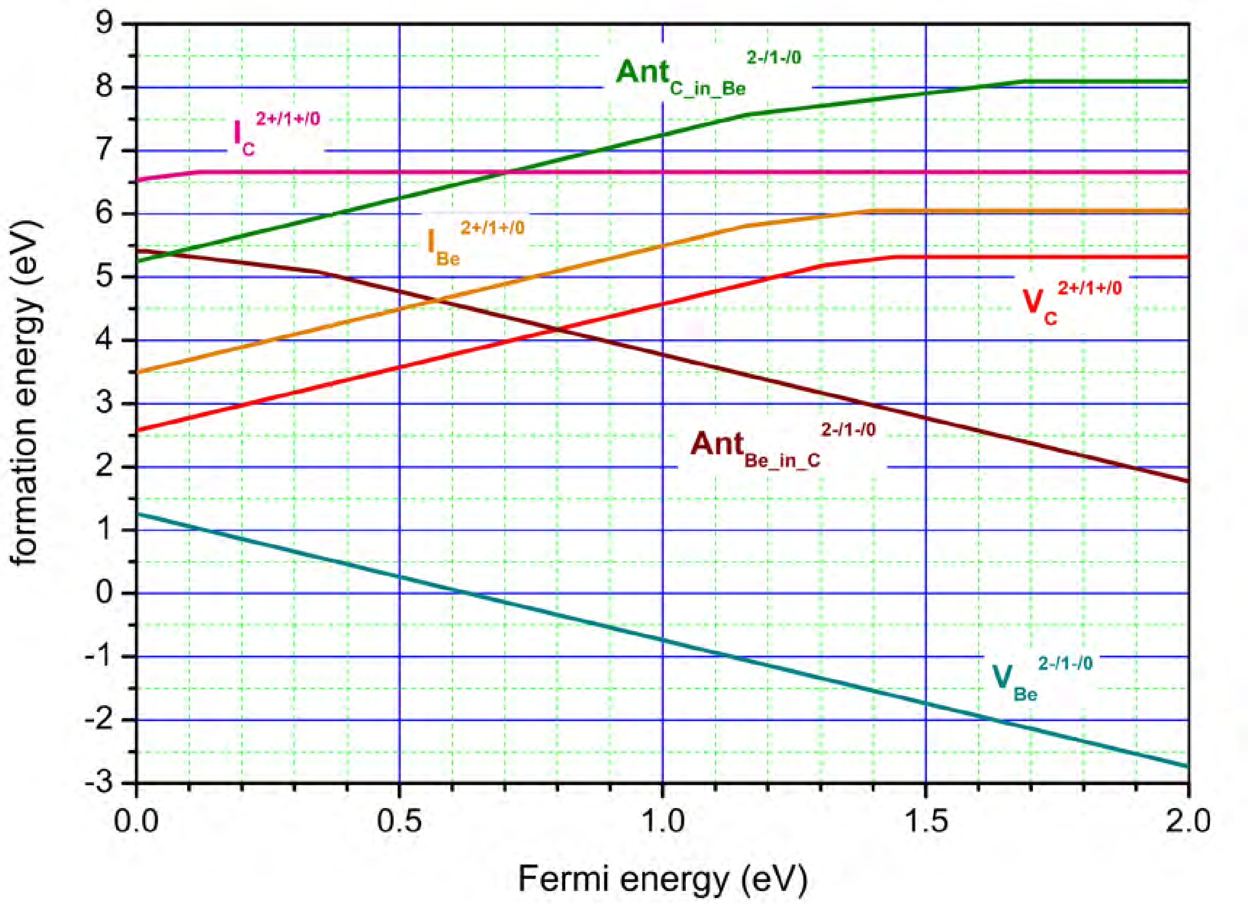
Point defects properties – energy formation

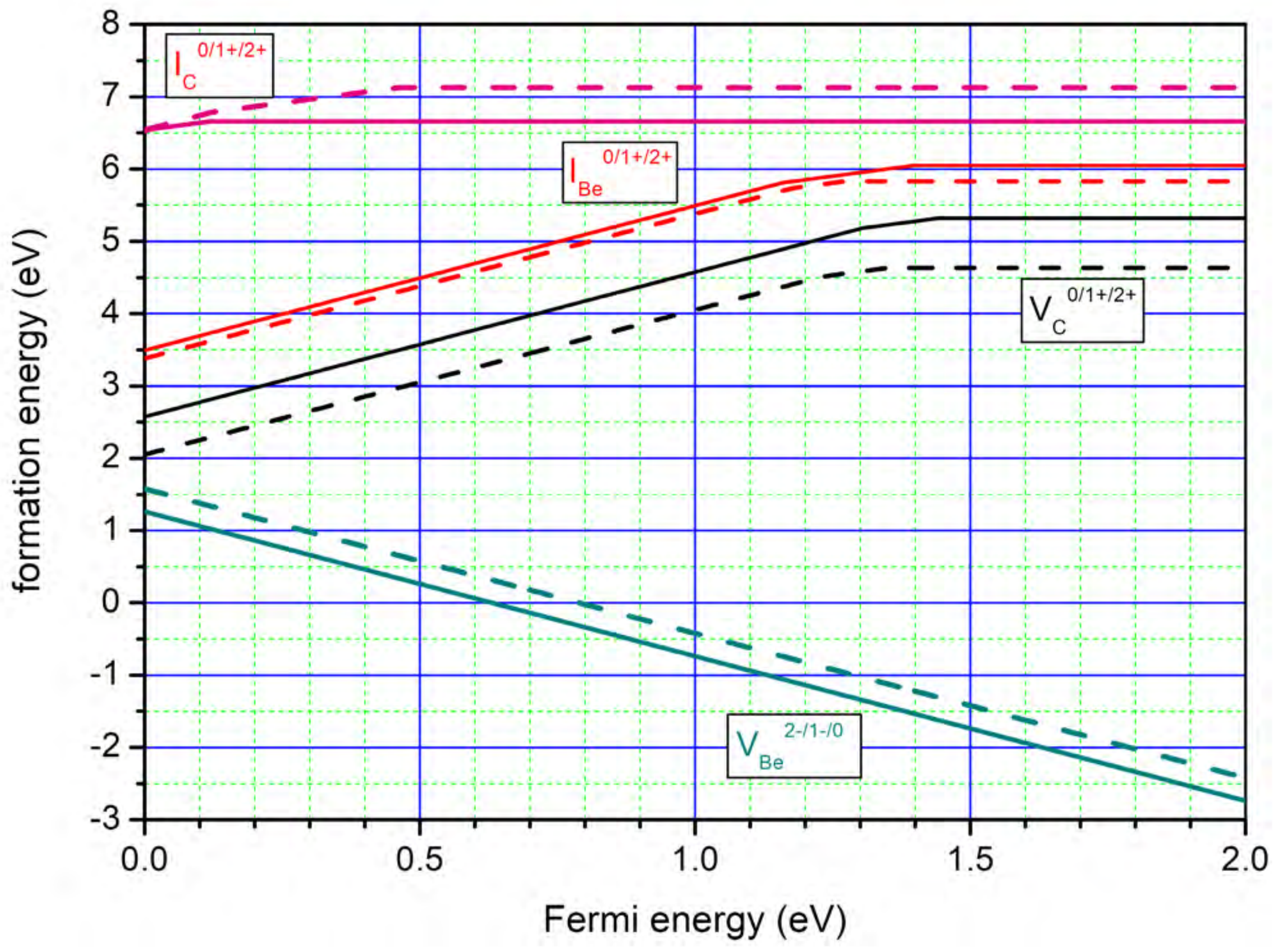
- **Formation energy of point defects strongly depends on their charge state;**
- **Defects presented in the plot :**

  I_c – C-interstitial atom
  I_{Be} – Be-interstitial atom
  V_C – vacancy in C-site
  V_{Be} – vacancy in B-site
  $Ant_{Be\_in\_C}$ – Be atom in C site
  $Ant_{C\_in\_Be}$ – C atom in Be site



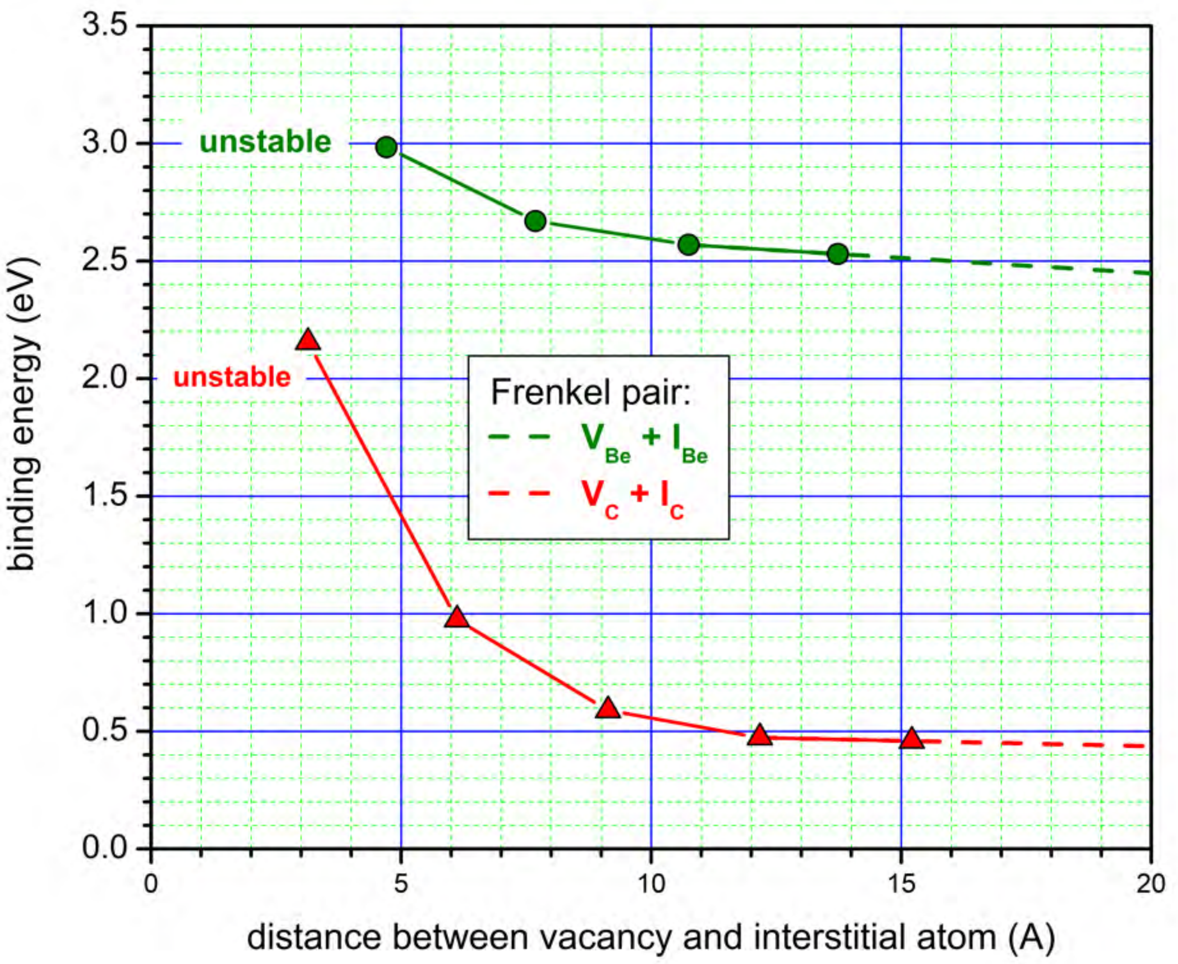
Point defects properties – model size effect

Vacancy and interstitial atom formation energies in the smallest, i.e. 3x3x3, (solid lines) and largest, i.e. 5x5x5, (dashed lines) supercells.



Point defects properties – Frenkel pairs

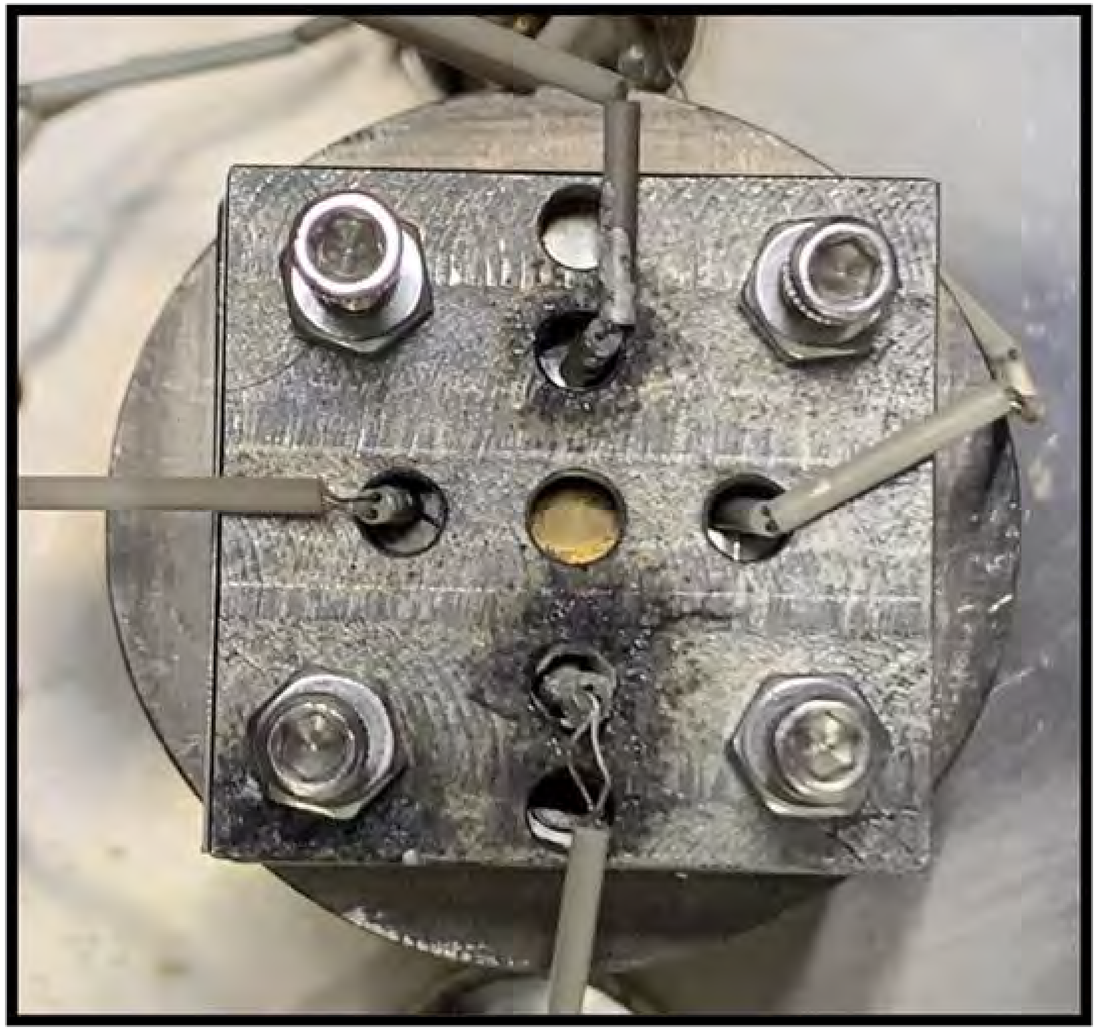
- **Be and C FP modelled in the large supercell 5x5x5 (1500 sites)**
- **Vacancy and interstitial atoms were separated by different distance along close to <111> direction.**
  - Pair in the first coordination spheres were unstable.
- **Binding energy was calculated relatively the neutral point defects:**
  - Reasonable for C-FP when energy drops to ~0.5 eV (instead of 0 eV)
  - Unlikely for Be-FP where energy saturates at ~2.5 eV



Ion Irradiation of Be_2C

Diego Múzquiz

Stephen Raiman



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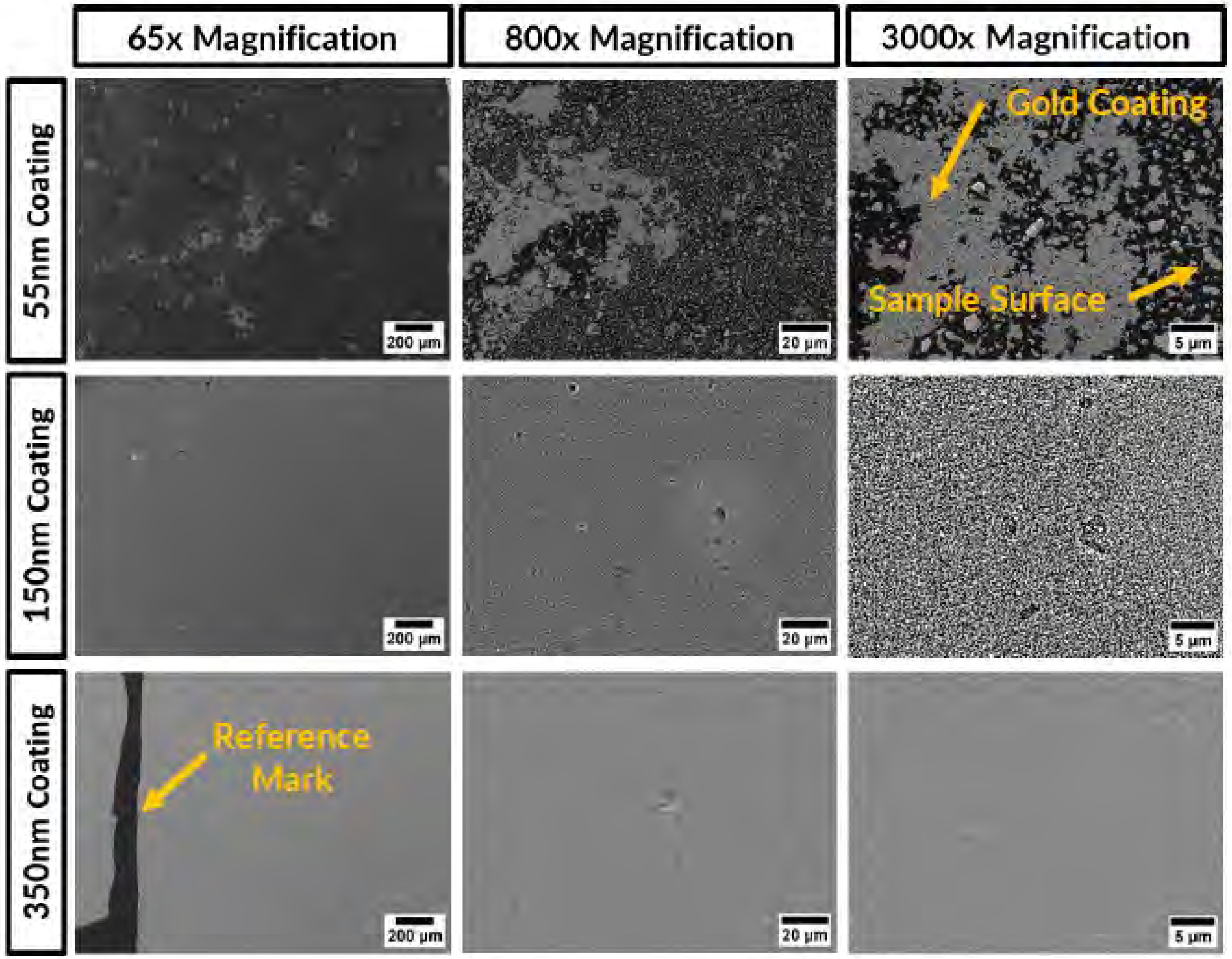
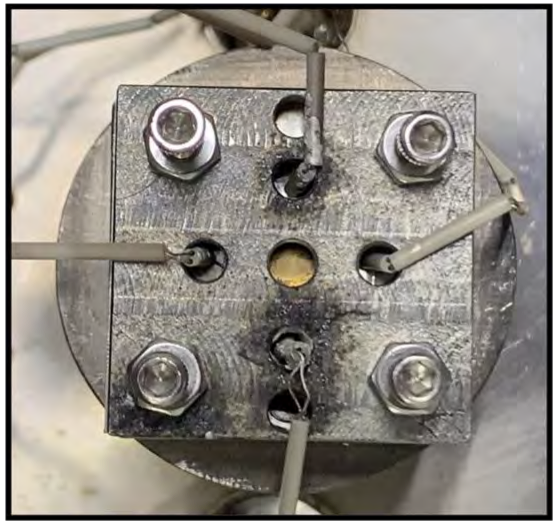
Primary Containment for Irradiations

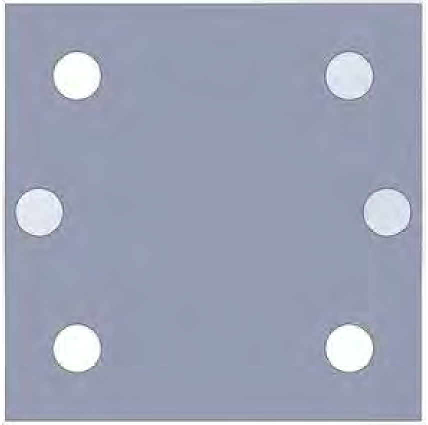
- **Irradiation parameters minimize sputter yield to an acceptable limit**
- **Gold Layer further reduces sample sputtering**
- **3 different coating were tested on SiC to support simulated results**



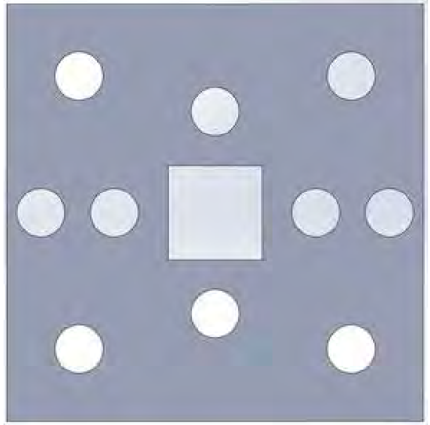
Secondary Containment Failsafe

- **Sample inside custom molybdenum box attaches to stage**
- **Molybdenum has high heat transfer while not melting at experimental temperatures**

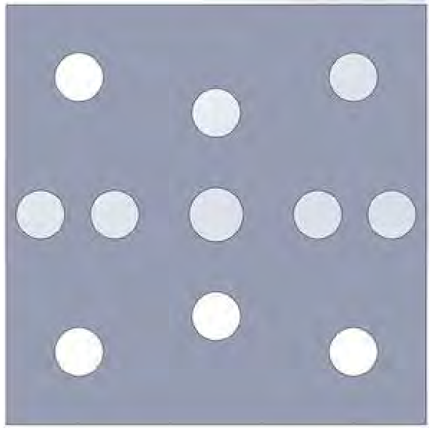




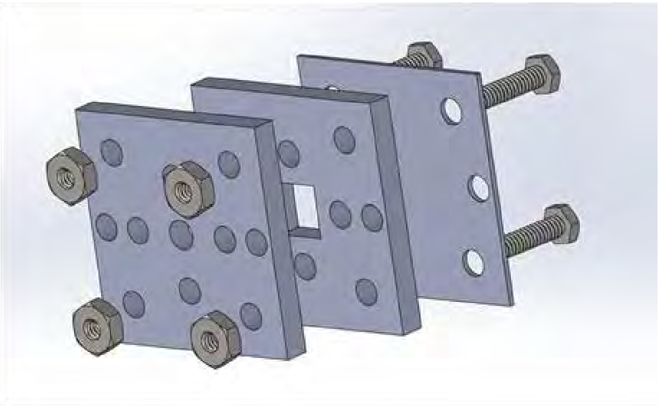
Thermal plate



Holding plate



Sputter plate



Assembly

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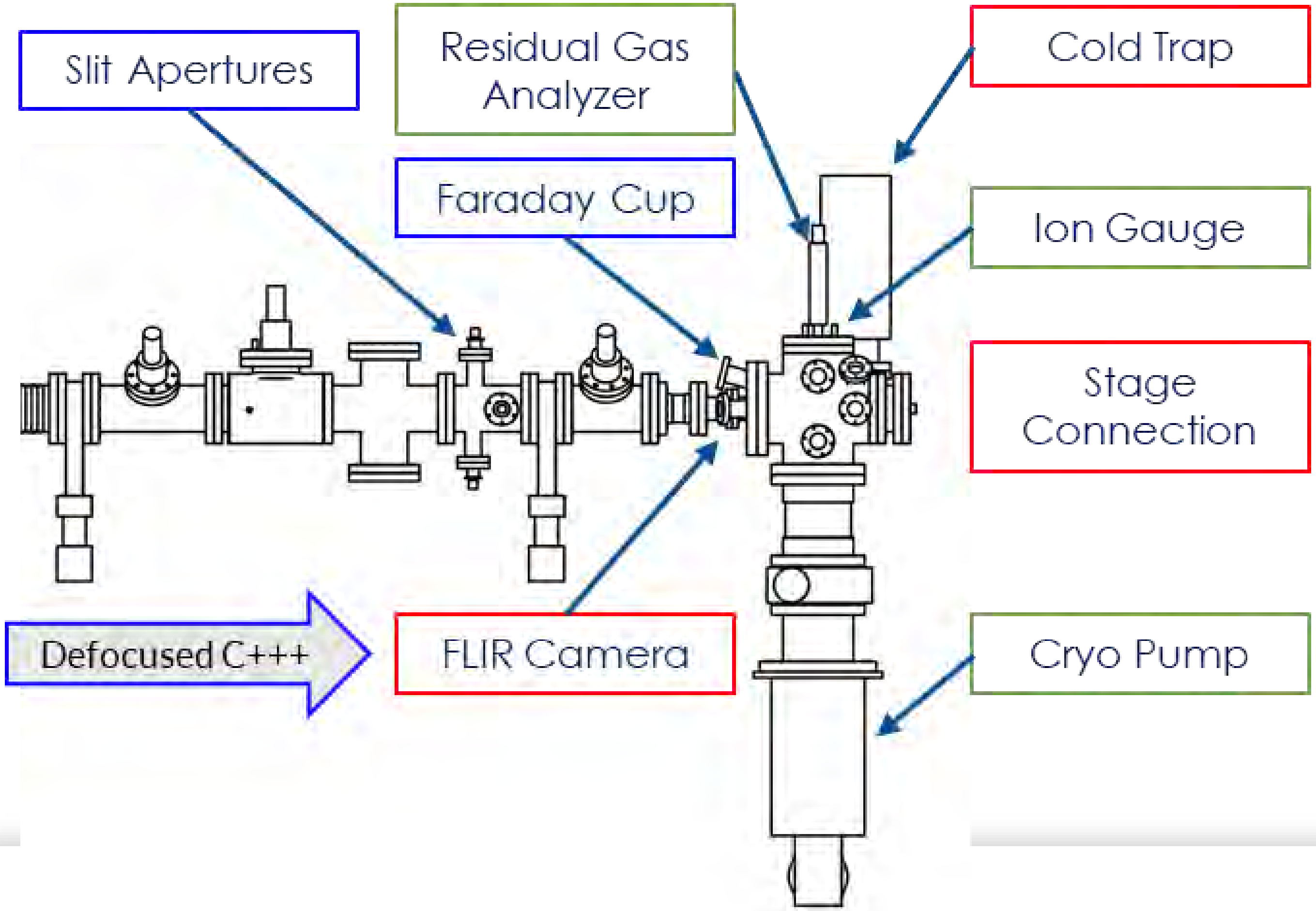
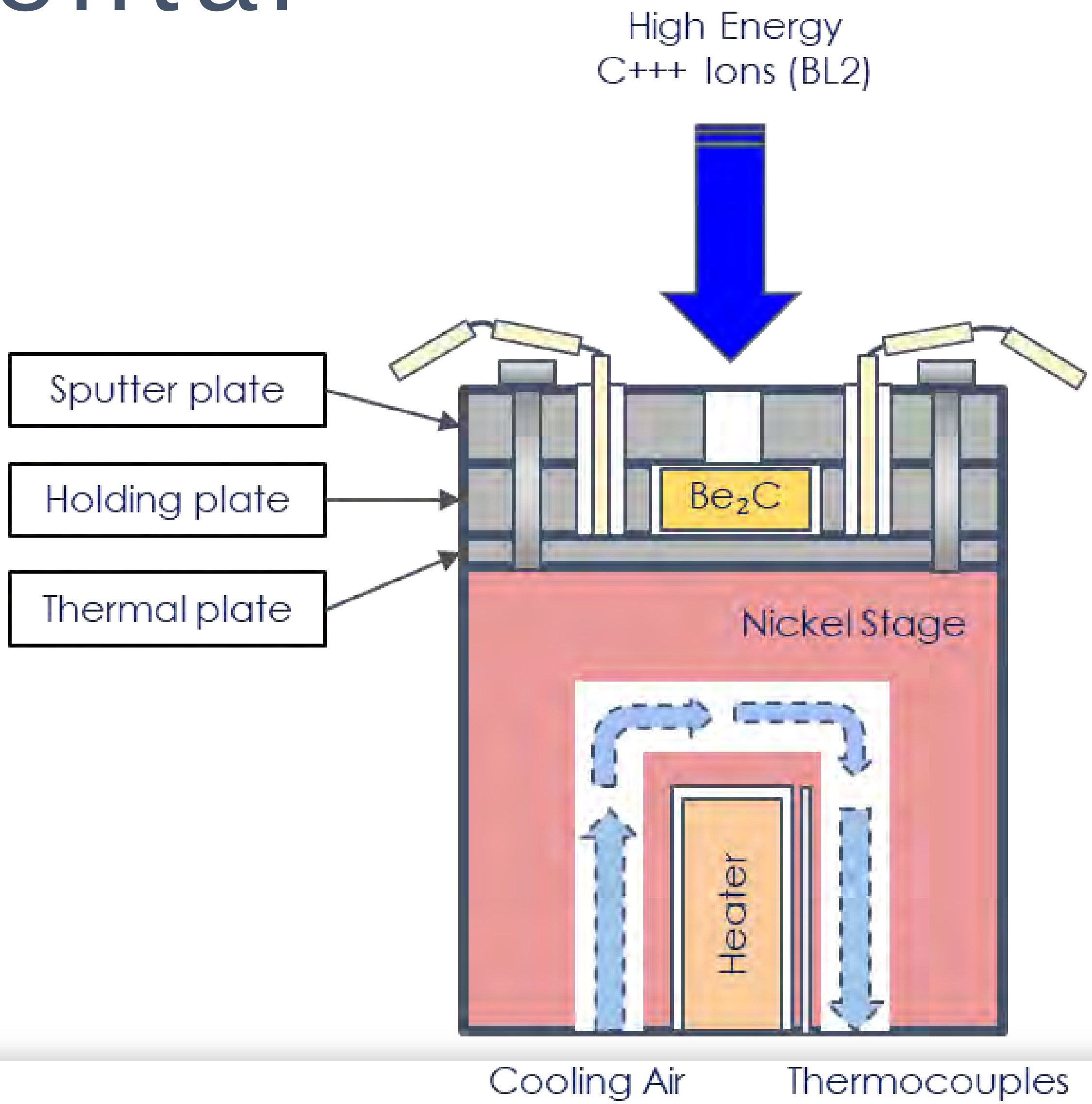
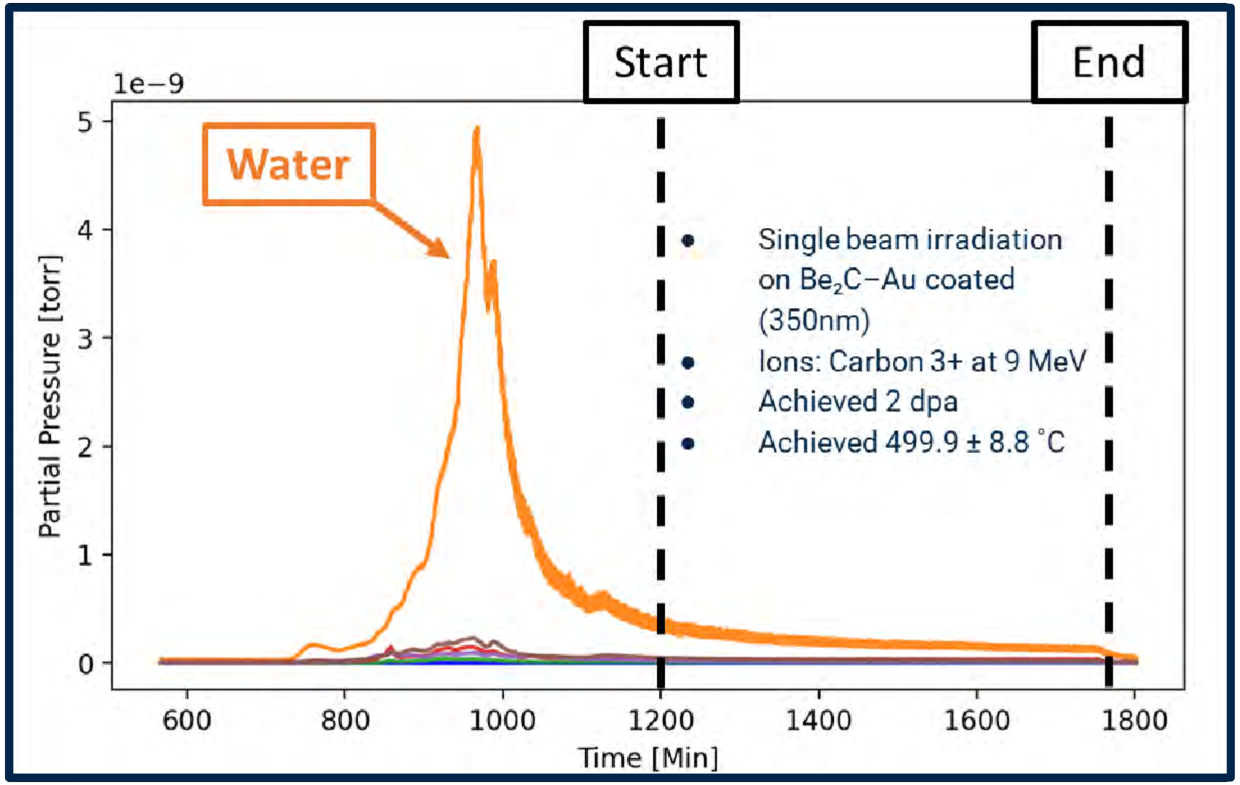
Irradiation Experimental Setup





Containment Monitoring and Swab Testing Post Irradiation

- **The RGA monitors the inside of the chamber**
- **Post irradiation, cleaning with a HEPA rated vacuum**
- **Swab tests are done post cleaning to ensure no beryllium remains**



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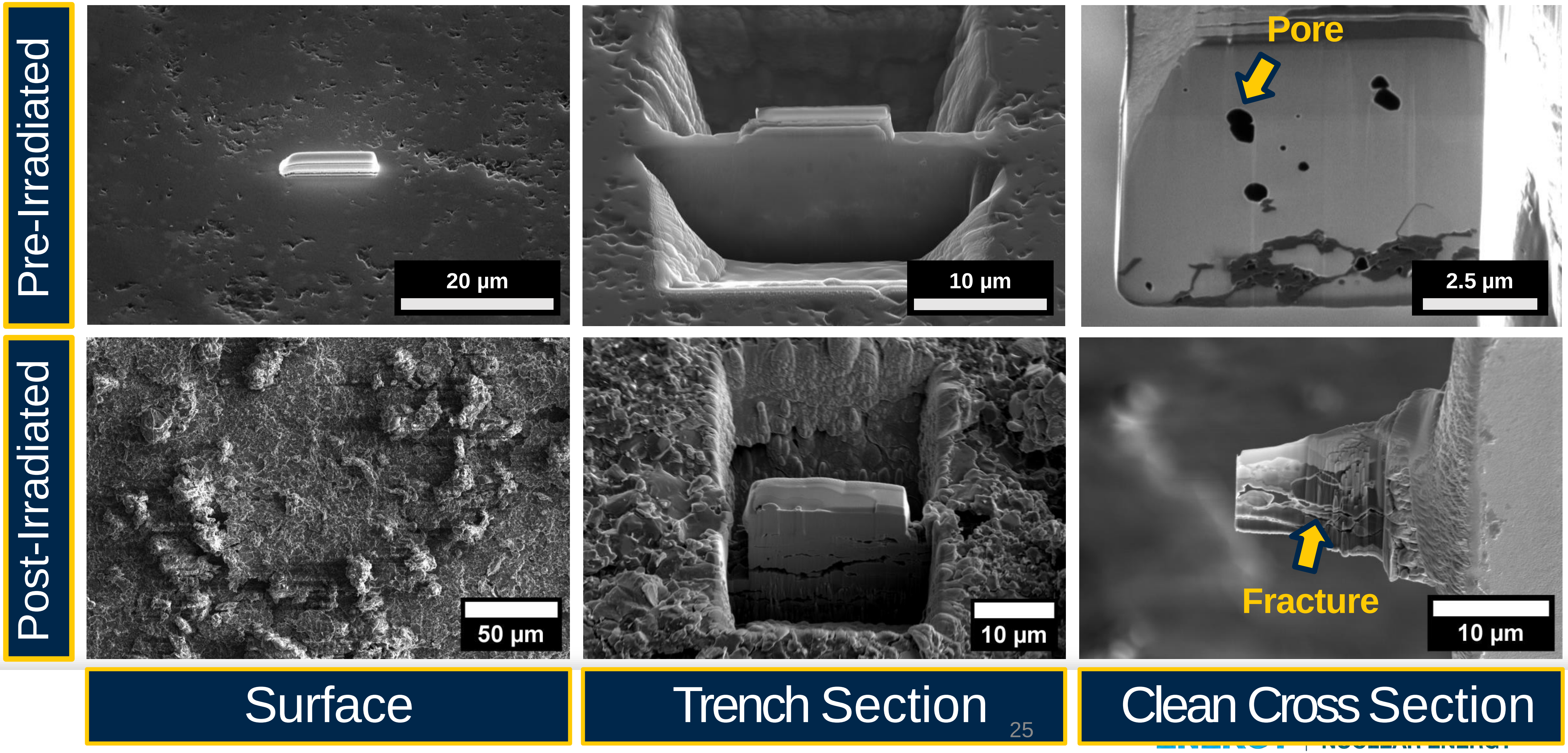
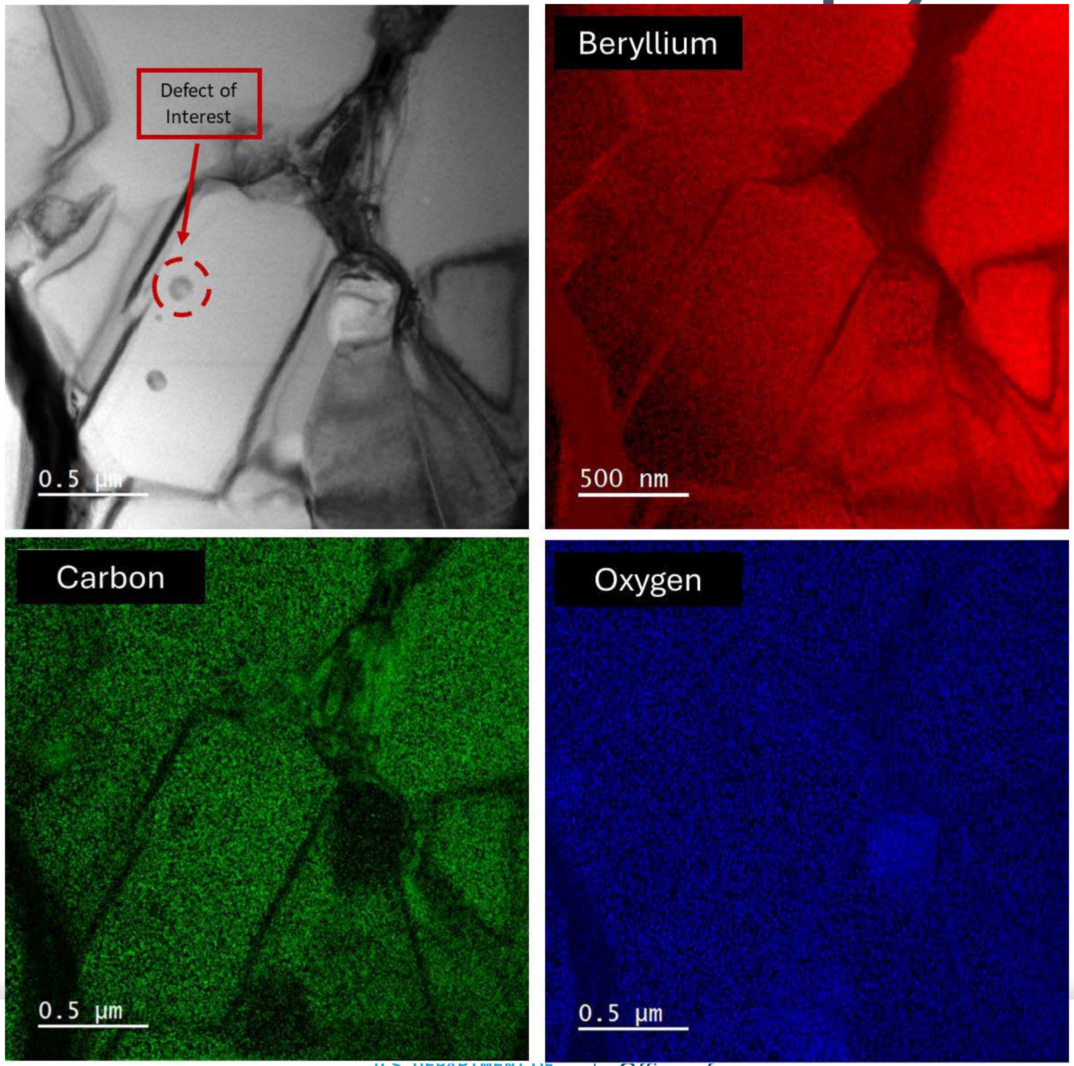
Scanning Electron Microscopy



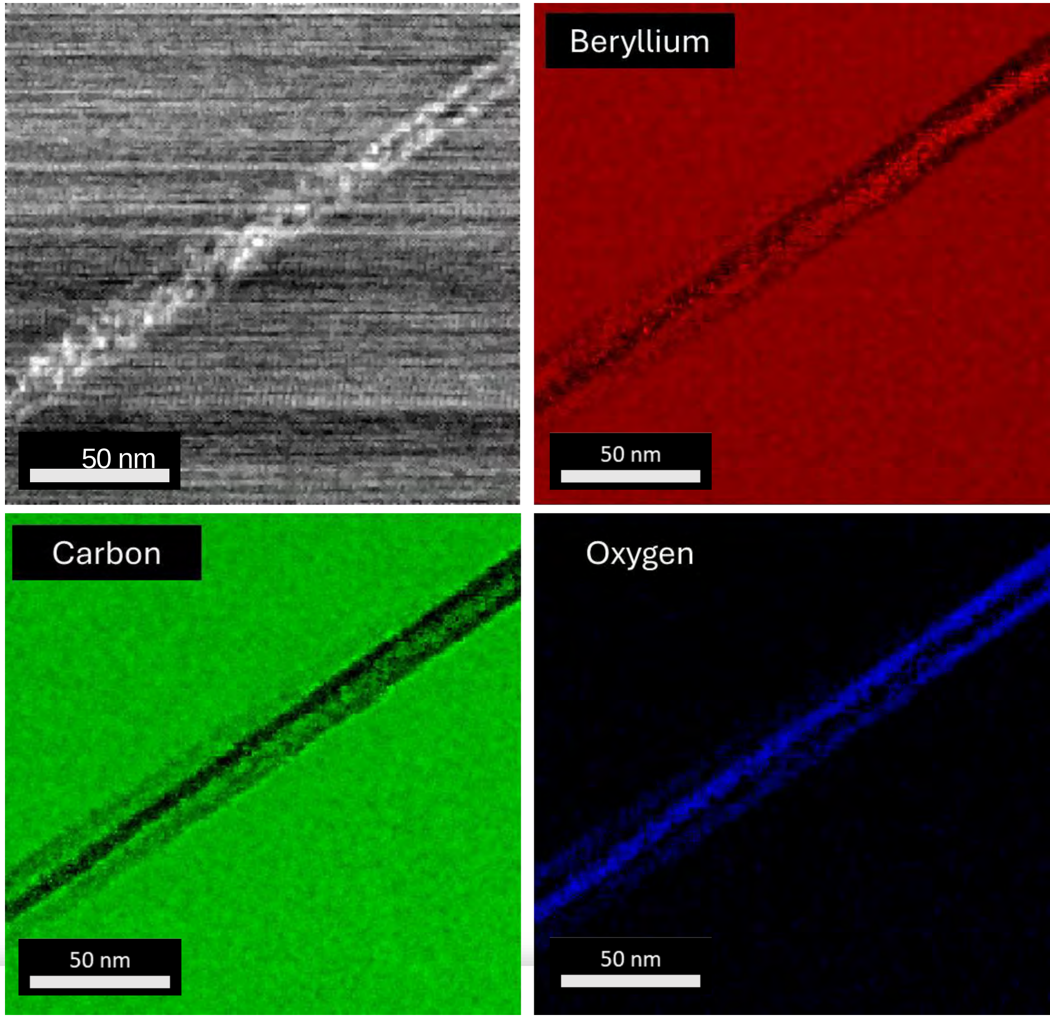
Transmission Electron Microscopy

- **5-month gap between experiment and examination**
- **Carbon depleted regions**
- **Oxygen rich areas**



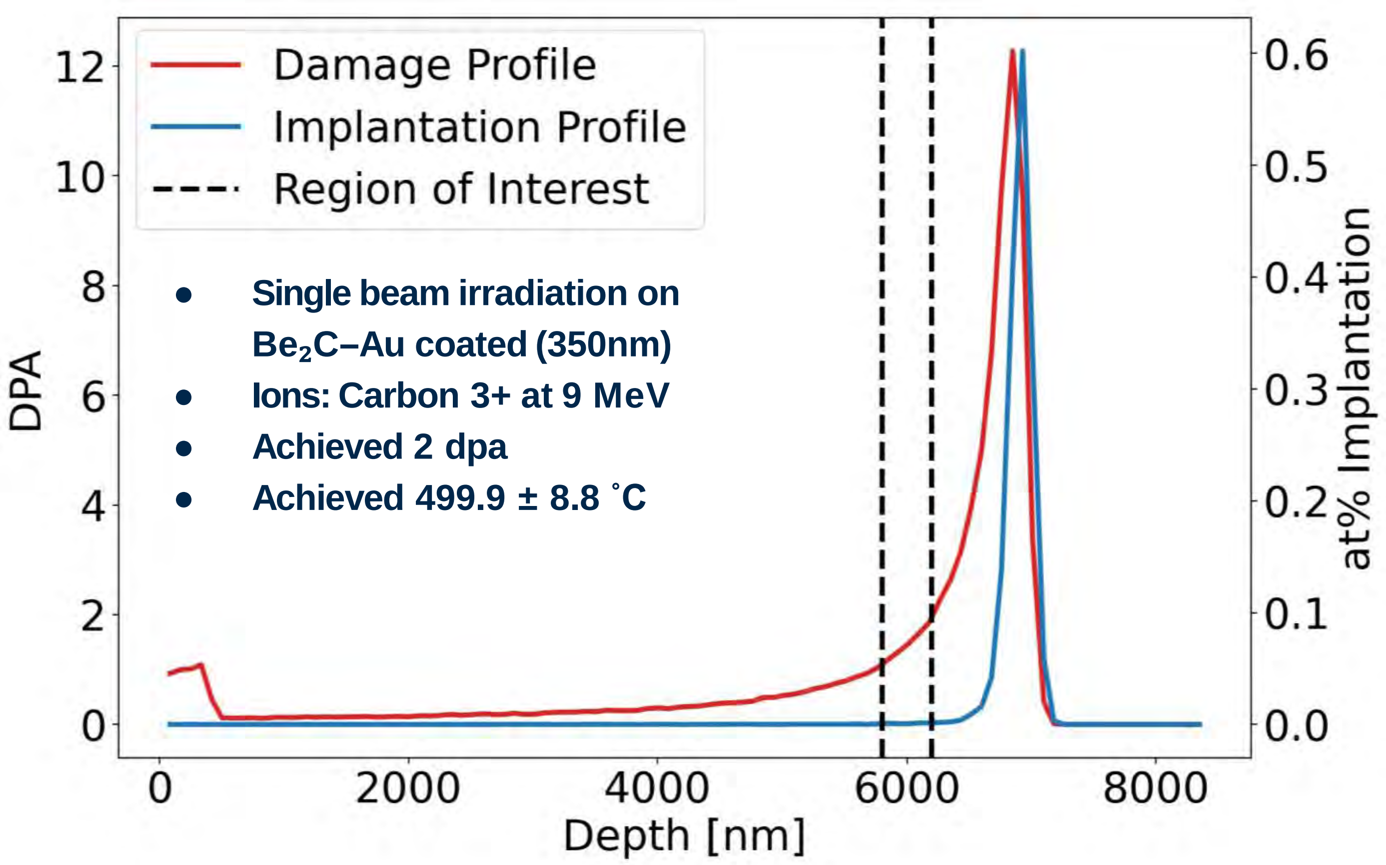
Crack Propagation from Oxidation

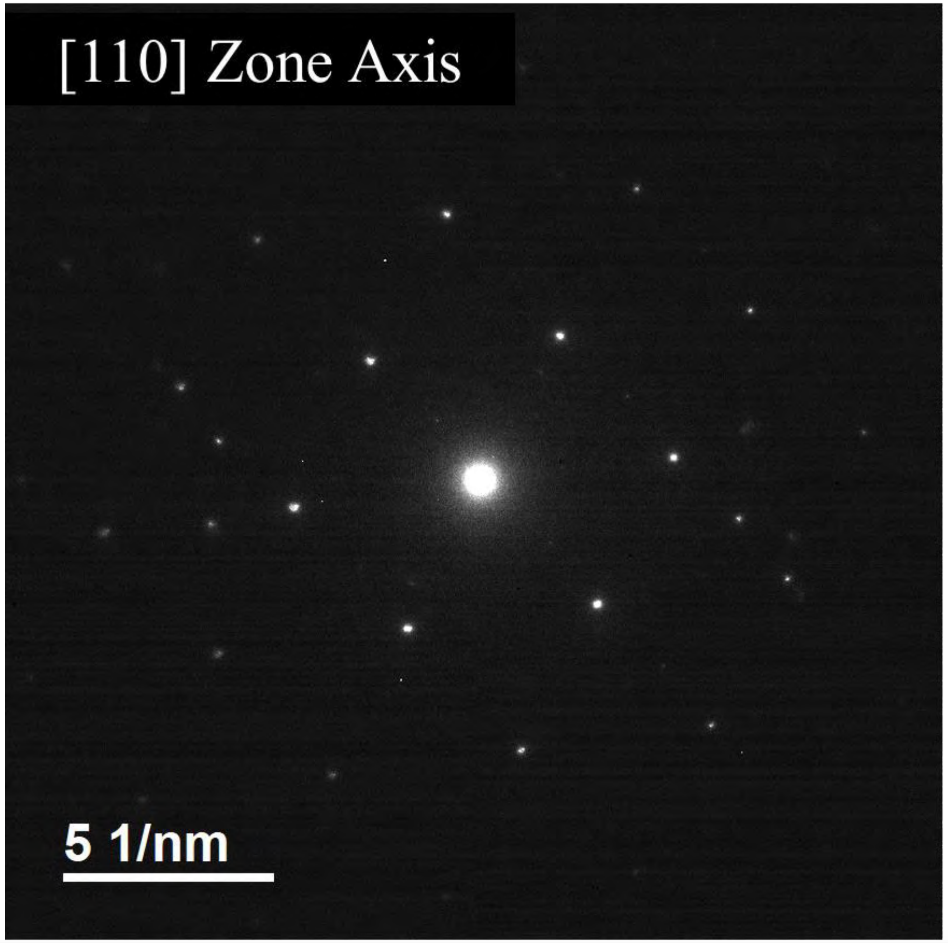
- $Be_2C + H_2O \rightarrow 2BeO + CH_4$
- **Methane form in exposed area**
- **Stress applied initiates cracks**
- **New surface area exposed**
- **Methane forms from new exposed area**



No Amorphization was Observed

- Single beam irradiation on Be_2C–Au coated (350nm)
- Ions: Carbon 3+ at 9 MeV
- Achieved 2 dpa
- Achieved 499.9 ± 8.8 ˚C





Upcoming Work

A. Willoughby

E. Cakmak

K. Johnson

B. Henry

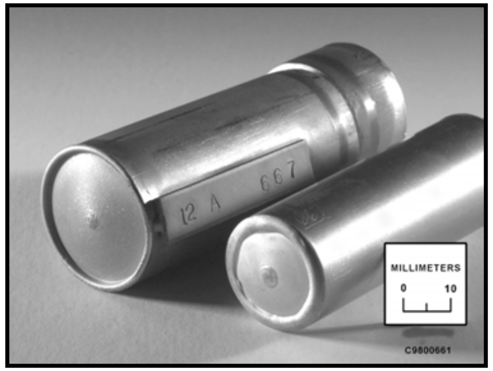
E. Paxton

S. Fiscor

High Temperature Stability

- **Already tested 650°C for 1 day, 1 week, and 2 weeks**
- **7 samples prepared and being measured via XRD for next set of exposures**
  - 600°C: 1 day, 1 week, 2 weeks, 1 month
  - 700°C: 1 day, 1 week, 2 weeks

Sample mounted on Mo capsule lid (courtesy J. Keiser)



Inner and outer capsules (courtesy J. Keiser)

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Degradation in hydrogen environment

- **Be_2C degrades to methane in the presence of hydrogen**
  - Can this be used for ^3H mitigation?
- **Small pieces of Be_2C will be exposed to controlled gas environments at 650°C (100% Ar, Ar + 1%H, Ar + 4%H)**
  - Quantify the rate of decomposition of Be_2C
  - Critical knowledge for future use in MSRs where hydrogen and tritium will be produced both by neutron capture in the solid Be and Be containing salts

Suggested future modeling activity

Understanding mechanisms of radiation damage and microstructure evolution assumes the following modeling activity:

- **Predicting diffusion:**
  - ✓ vacancy – vacancy jump barriers and kinetic Monte Carlo modeling vacancy diffusion;
  - ✓ interstitial atoms – because of the complexity of diffusion mechanisms, direct molecular dynamics modeling should be applied;
- **Defect-defect interactions:**
  - ✓ dilatation properties of vacancy and interstitial defects needed for long-range interaction in strain fields;
  - ✓ extended defects nucleation and growth mechanisms and energy and structure properties;
  - ✓ charge effects in defect-defect interactions;
- **Development of kinetic Monte Carlo model for the overall dynamics of microstructure evolution.**

Additional Ion Irradiation Studies

- 30 dpa (going on right now)
- Use ion implantation to study H and He diffusion characteristics
- In-Situ dual-beam irradiation (C^+ with simultaneous H implant)
- Static and flowing FLiBe exposures

Beyond FY24

- **From these preliminary results evaluate if a neutron irradiation campaign is viable. Discussing with AMMT about this work as it now is part of the AMMT portfolio going forward**
- **Work with Materion to develop advanced processing methods to tailor material properties**
- **Any future work will require setup of capabilities for handling and testing solid Be_2C both pre- and post-irradiation**
  - Glove boxes, testing equipment (mass/dimensions, elastic properties, strength, CTE, thermal diffusivity, etc.)

Thank you

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