Enhancing Lifetime of Environmental Barrier Coatings for Hydrogen-Fired Industrial Gas Turbines

M. J. Ridley, M. J. Lance, T.G. Aguirre, B. A. Pint
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

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  - J. Horenburg – metallography
  - T. Lowe – SEM
  - Y. Su – TEM
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- Collaborations
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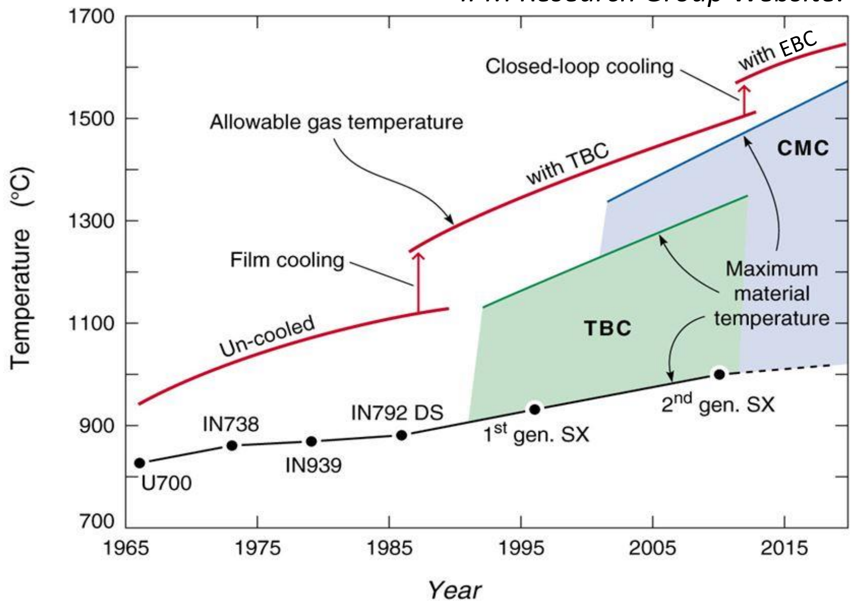
  - NASA Glenn Research Center (K. Lee)
  - 2 industrial collaborators

Enabling ceramic matrix composites (CMCs) for combustion environments requires protective environmental barrier coatings (EBCs)

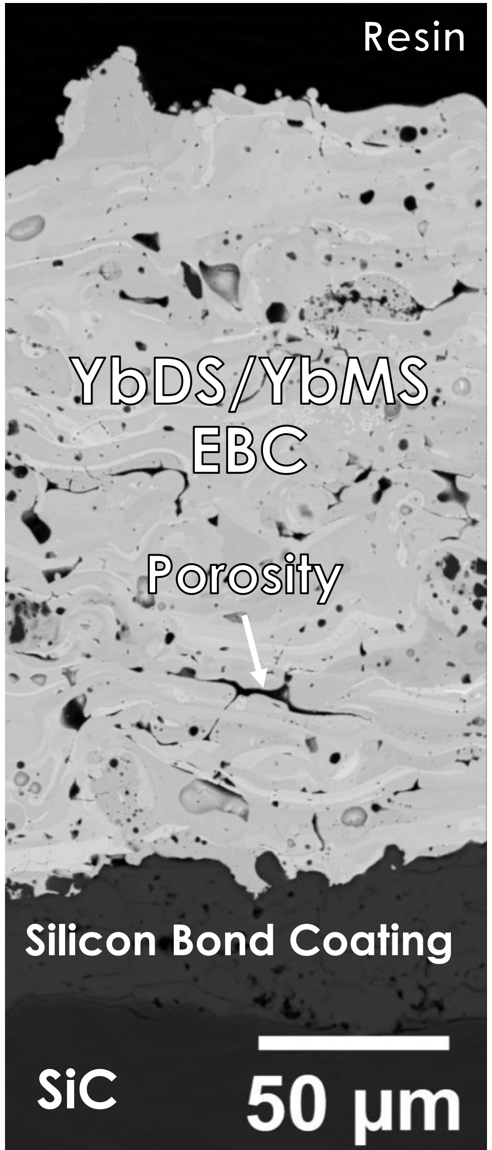
- CMC components entered commercial service in 2016 (GE/Safran LEAP engine)
  - $1/3^{rd}$ the density of traditional superalloys
  - High-temperature stability + strength
  - SiC recesses in steam environments
- Interest in CMCs as hot section components for land-based turbines
  - H_2 / H_2 blend fired IGTs to replace natural gas for green power production
  - Turbine efficiency increase likely needed to offset H_2 (g) costs
  - Increased temperatures and steam production

IPM Research Group Website.



Foundation: Environmental Barrier Coatings (EBCs) needed to protect SiC in combustion environments

*$Yb_2Si_2O_7$ (YbDS) EBCs are research standard



1. **SiC oxidizes in air/steam environments**
   - $SiC + 2O_2\ (g) = SiO_2 + CO_2\ (g)$
2. **SiO_2 volatilizes in steam environments**
   - $SiO_2 + 2H_2O\ (g) = Si(OH)_4\ (g)$

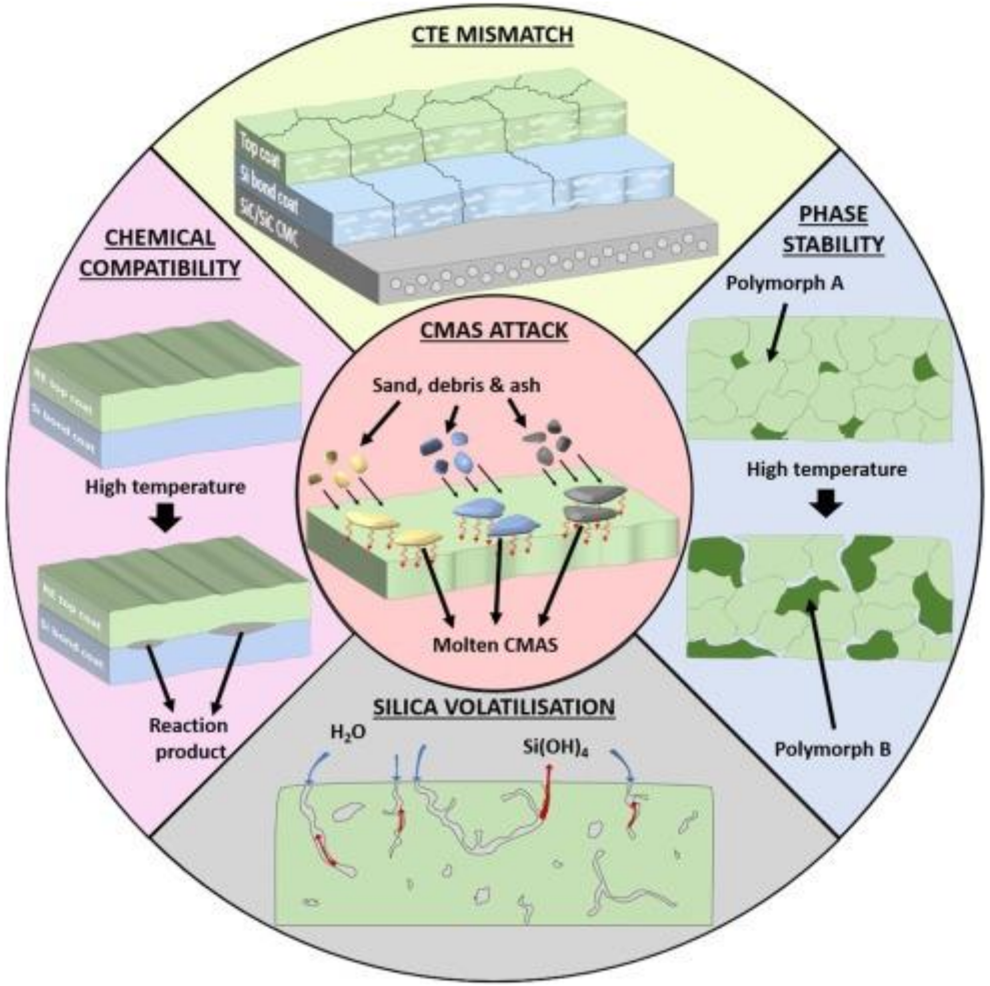
Oxidation must be minimized for long lifetimes **(1)**

EBCs required to prevent volatilization **(2)**

SiC/SiC shroud with EBC
General Electric, DOE's Continuous Fiber Ceramic Composite (CFCC) program

EBC failure modes need to be better understood for long term IGT application

- Steam reaction: Si-based ceramics volatilize in steam
- **Bond Coat Oxidation: Weakens interface, promotes delamination**
- Thermal Stability: Phase/property changes during operation
- Thermal Expansion Mismatch
- CMAS: Infiltration of molten particulate ingested into engine
- Foreign Object Damage



Tejero-Martin et al., J. Eur. Cer. Soc. (2021).

Themes for ORNL EBC Lifetime Model Development

1. Perform cyclic steam oxidation tests to measure oxidation kinetics
   - Baseline EBC ($Yb_2Si_2O_7$) and initiation of modified EBC chemistries
   - EBC/CMC systems without the Si bond coating
2. Finite element model to guide understanding of failure modes
   - Thermal expansion coefficients measured for implementation
   - SiO_2 phase change included in simplified model
3. Use advanced characterization tools to identify leading cause for coating failure
   - SiO_2 phase transformation and growth rate

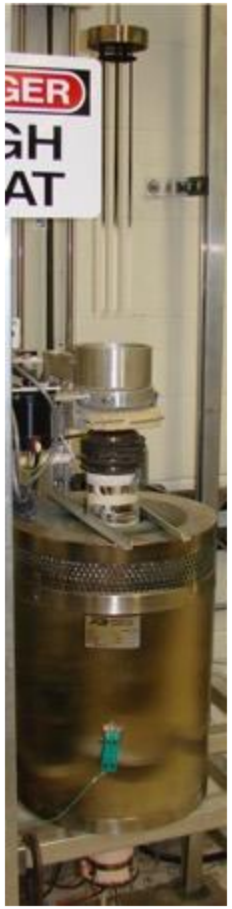
Capabilities: Focus on cyclic steam furnaces

1-h cycles: automated cyclic rigs
Air + 90%H_2O, 10 min cool in lab. air

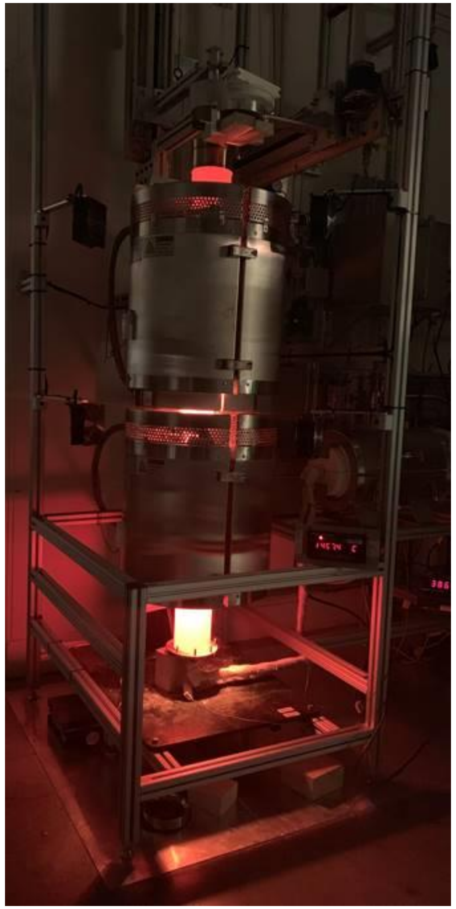
- 1-h or 100-h thermal cycling
- SiC or Al_2O_3 labware
- 1.5 cm/s or 10 cm/s
  - TGO growth underneath EBC not strongly dependent on gas flow rate above EBC

lid

furnace



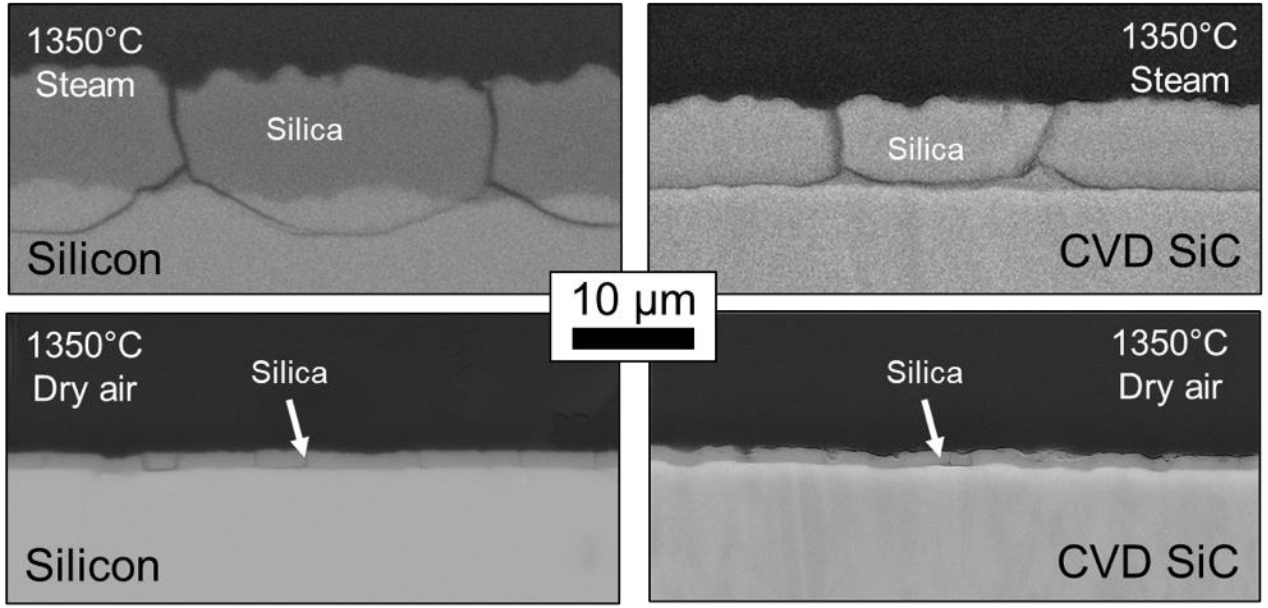
2005 cyclic rig:
1350°C maximum



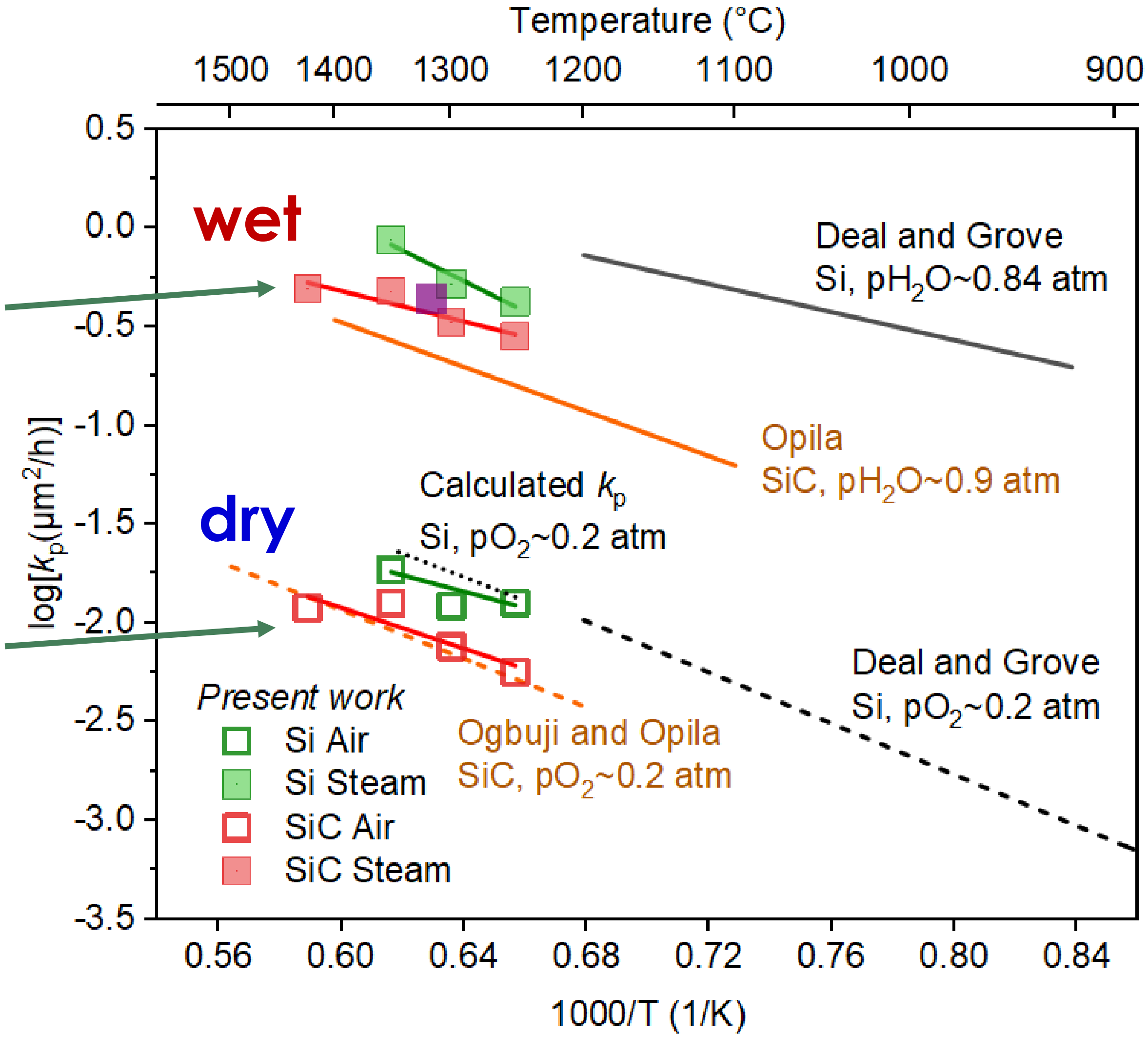
2019 cyclic rig:
1500°C maximum

Methodology for assessing EBC performance is based on bare SiC/Si oxidation in air and steam

Silica in steam: EBCs to prevent evaporation – $Si(OH)_4$ AND reduce scale growth rate



Experiments performed in SiC reaction tube



Kane, et al. *J. Amer. Ceram. Soc.* 105 (2022) 590

- Based on Harder (NASA)
- Defines upper and lower bounds for EBC performance

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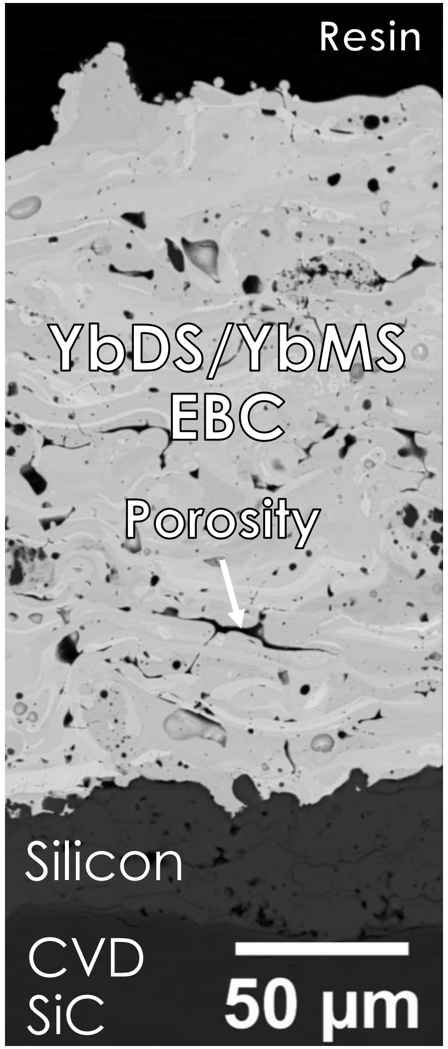
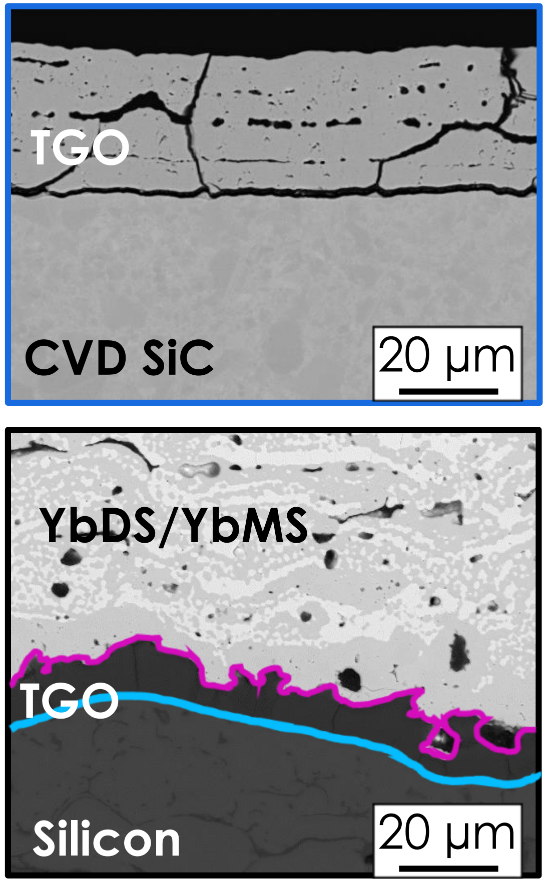
Methodology & Software developed for assessing EBC performance is based on bare SiC/Si oxidation in air and steam

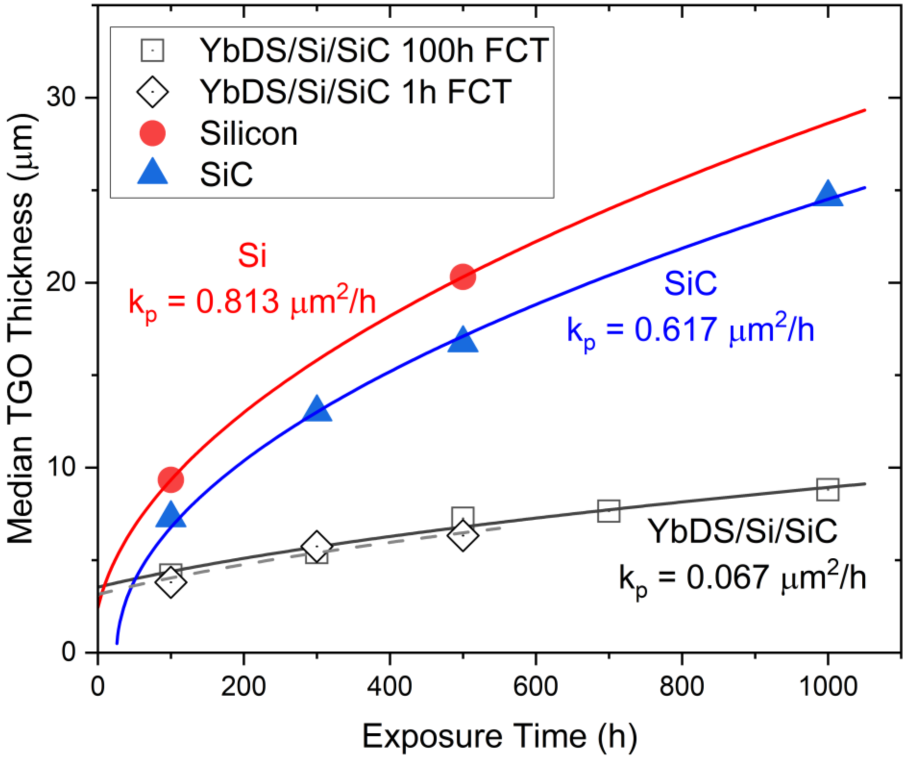
Starting Material (Stony Brook University)



1000h Exposure 1350°C, 90% H_2O (g)



Parabolic oxidation kinetics



ORNL open-source code developed for SiO_2 growth

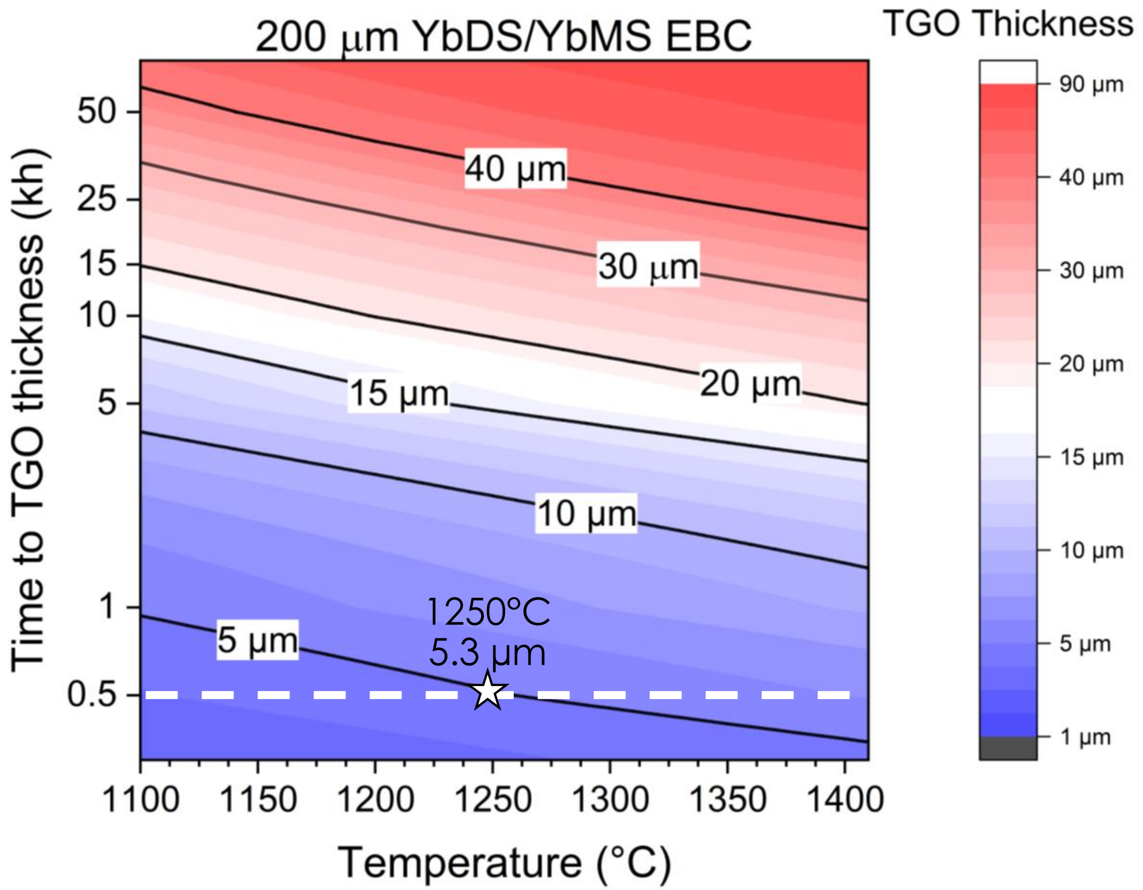
https://github.com/TriplePointCat/SOFIA-CV

High statistics: thousands of measurements over mm's of cross-section

Su Y.-F., et al. **OnePetro**. (2021).

Big Picture: Develop Lifetime Model for Industrial Gas Turbine EBCs

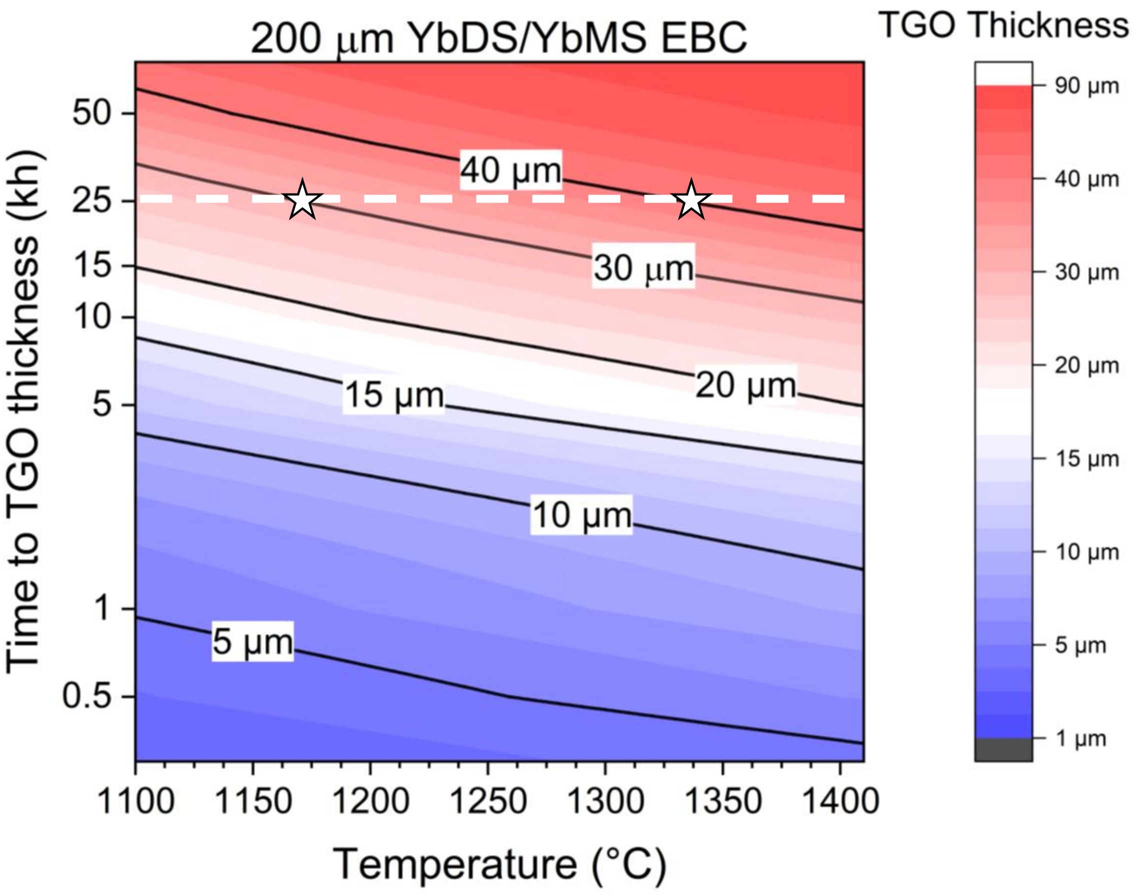
- *Kinetics*: Use intermediate timescale kinetic data to estimate maximum operating temperature for achieving 25k hours of service time
  - 1350°C, up to 1000h test data
- *Thermodynamics*: Temperature dependence for Si oxidation
- **Model validates test data at other temperatures (ex. 1250°C)**



Exposure Time	Model Predicted (µm)	Measured (µm)
100	2.2	2.7
300	3.6	3.9
500	5.0	5.3
Rate	0.051 $\mu m^2/h$	0.052 $\mu m^2/h$

Big Picture: Develop Lifetime Model for Industrial Gas Turbine EBCs

- Predictive quality can be improved with further testing
- Does not incorporate microstructure or pressure effects
- **Is there a critical TGO thickness for EBC failure?**
  - 30 µm TGO, max temp: 1170°C
  - 40 µm TGO, max temp: 1334°C
  - Likely governed by system stresses, cracking, bond strength, microstructure evolution



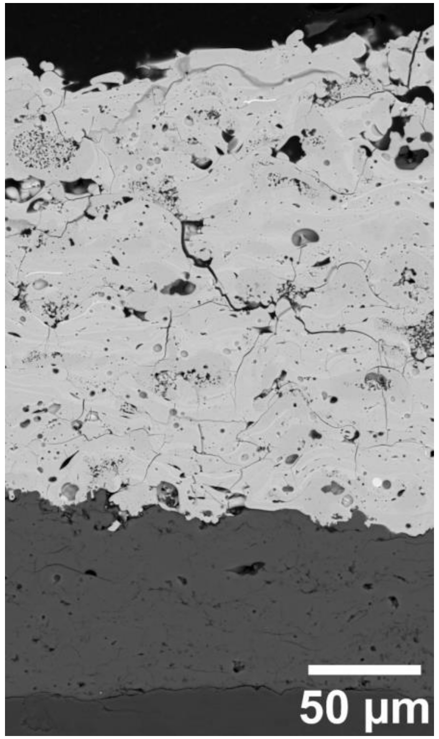
Improvements needed for lifetime model (2024 – 2026)

1. **How do dopants impact oxidation resistance?**
2. **What is the critical SiO_2 thickness for EBC failure?**

Initial laboratory studies on modified EBC systems to improve performance

Provided by:
Comm. Partner 1

(Y/Yb)DS

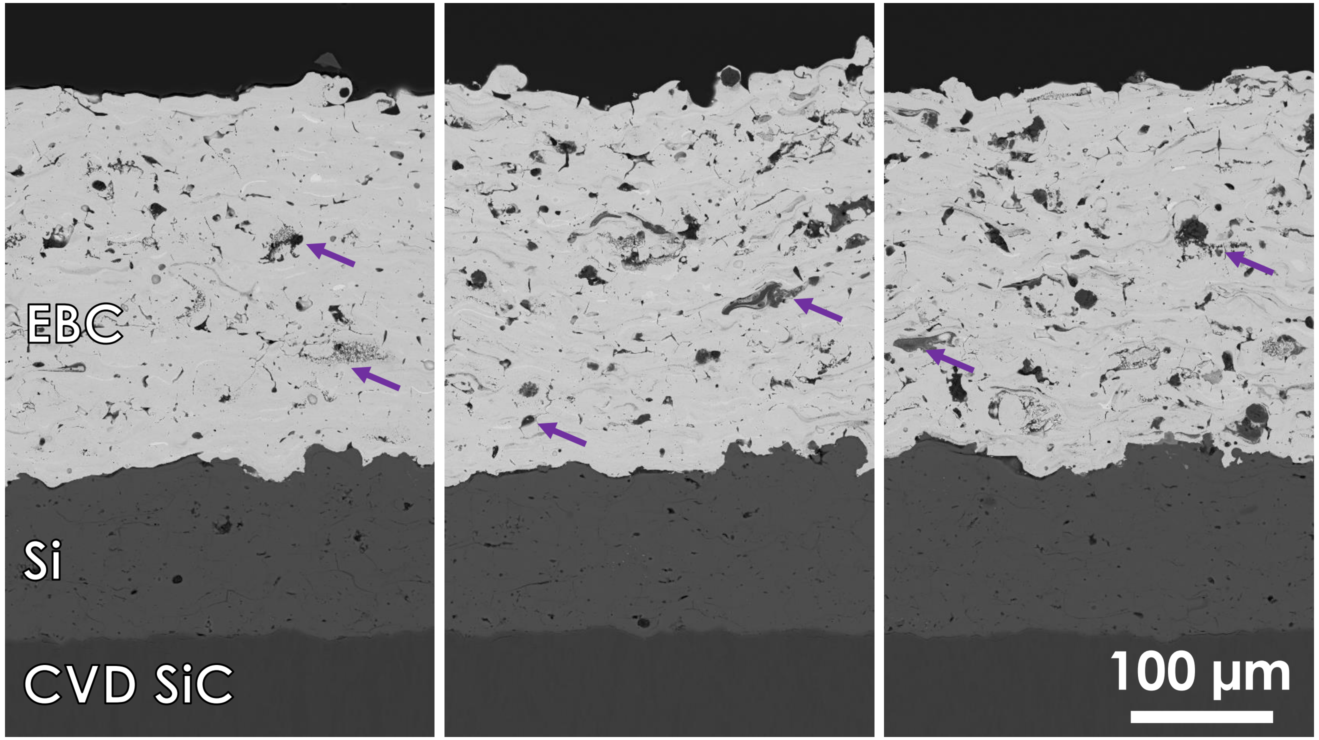


Commercial EBC

Dopant:
$Y_2Si_2O_7$

Provided by:
NASA Glenn Research Center

YbDS+D1 | YbDS+D2 | YbDS+D3

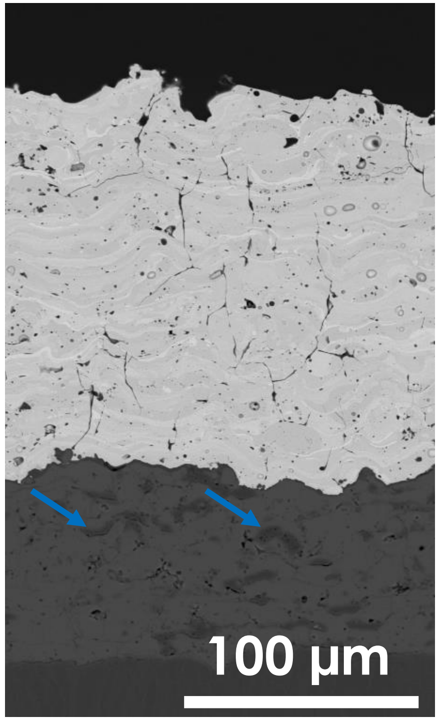


Inc. Concentration of Dopants in EBC

Dopants (D):
Mullite, $3Al_2O_3$-$2SiO_2$
YAG, $Y_3Al_5O_{12}$

Provided by:
Comm. Partner 2

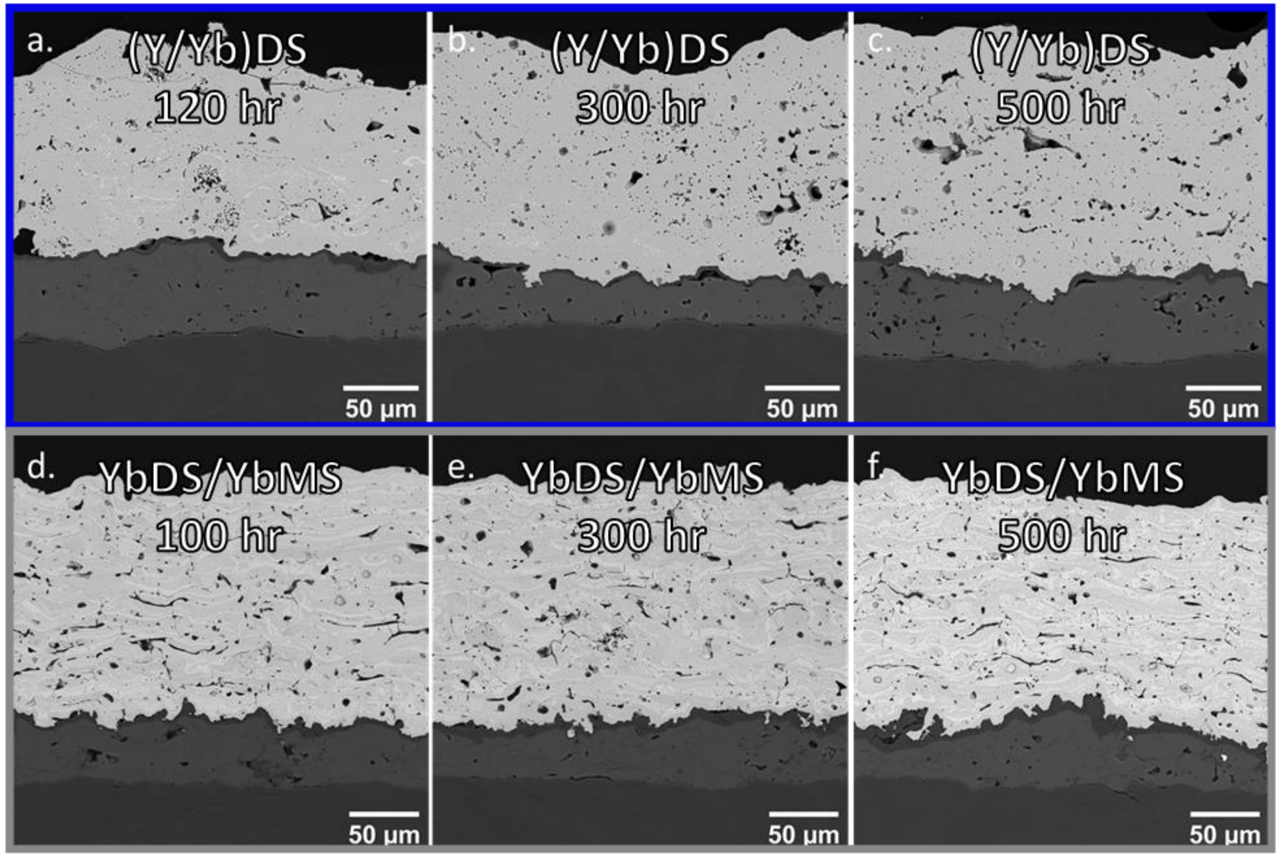
YbDS/YbMS

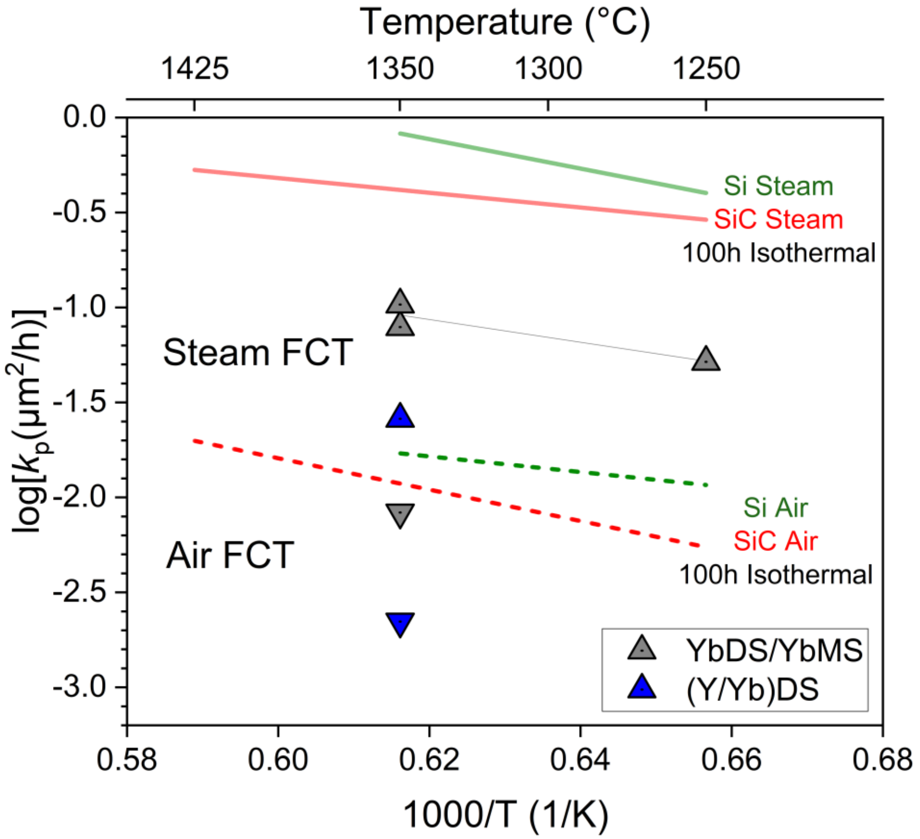


Dopants in Si

Dopant:
Al_2O_3

Commercial (Y/Yb)DS has lower rates than YbDS in both air and steam (2021-2022)



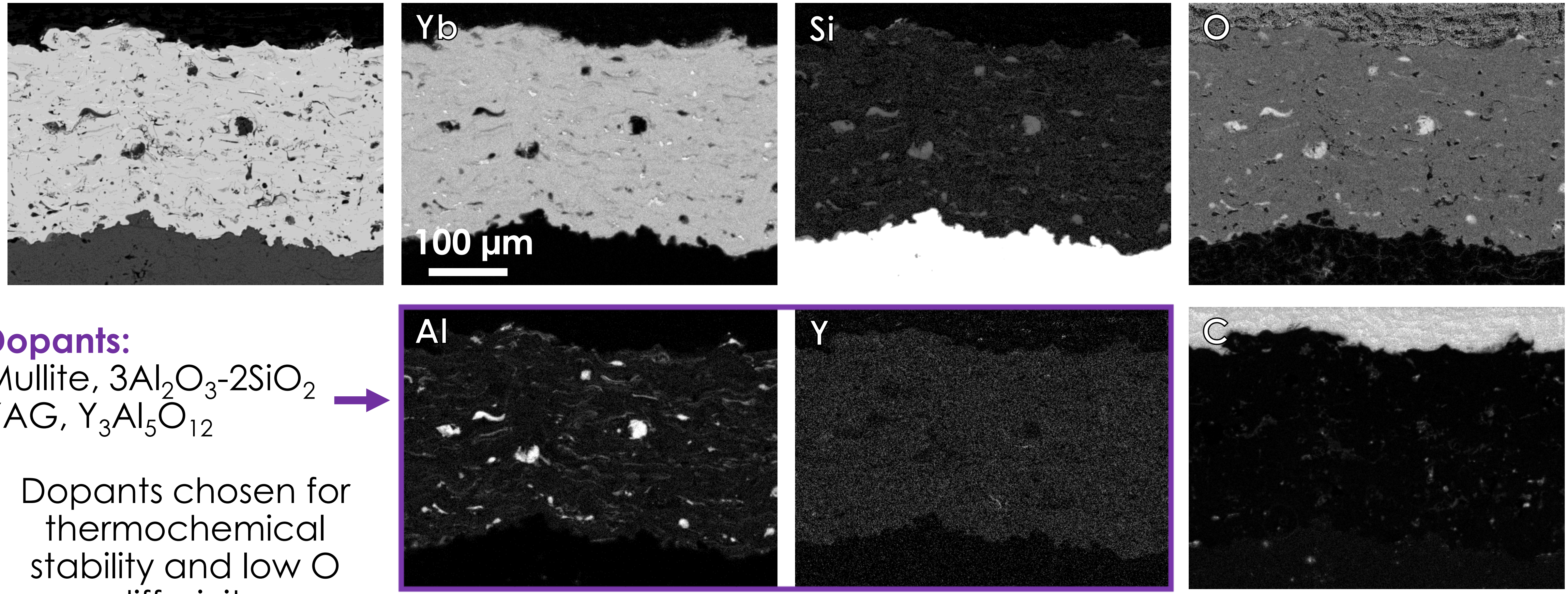


- Why (Y/Yb)?: $16.4/kg Yb_2O_3, $3.4/kg Y_2O_3
- Manufactured at different locations, one temperature: further study needed
- Stony Brook Univ. spraying (Y/Yb)DS EBCs with commercial powder (FY24)

Ridley, MJ, et al. JACERS. (2022).
Stack, P, et al. JECERS. (2022).

Three doped EBC compositions received through collaboration with NASA Glenn Research Center (2023)

Research-grade EBC with dopants: **YbDS+D3 EDS Mapping**

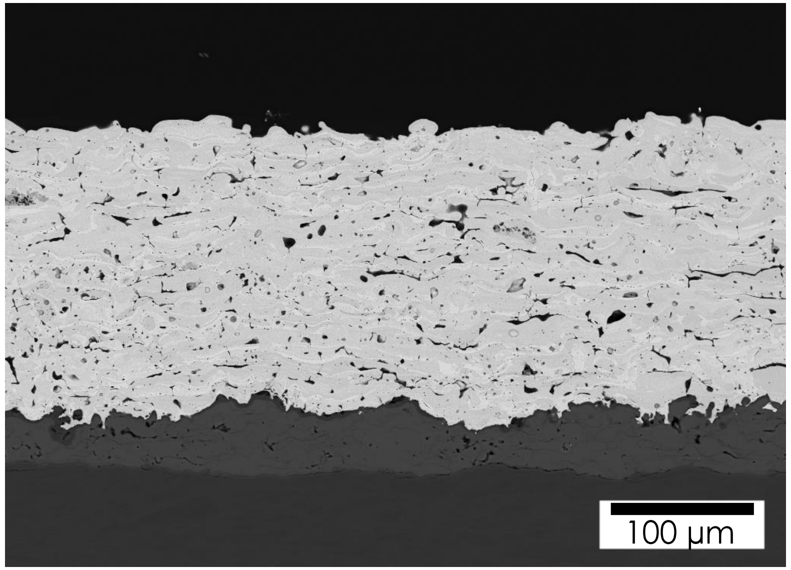


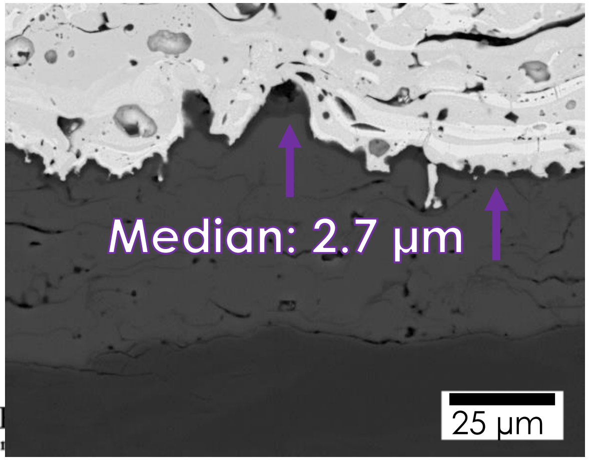
Dopants:
Mullite, $3Al_2O_3$-$2SiO_2$
YAG, $Y_3Al_5O_{12}$

Dopants chosen for thermochemical stability and low O diffusivity

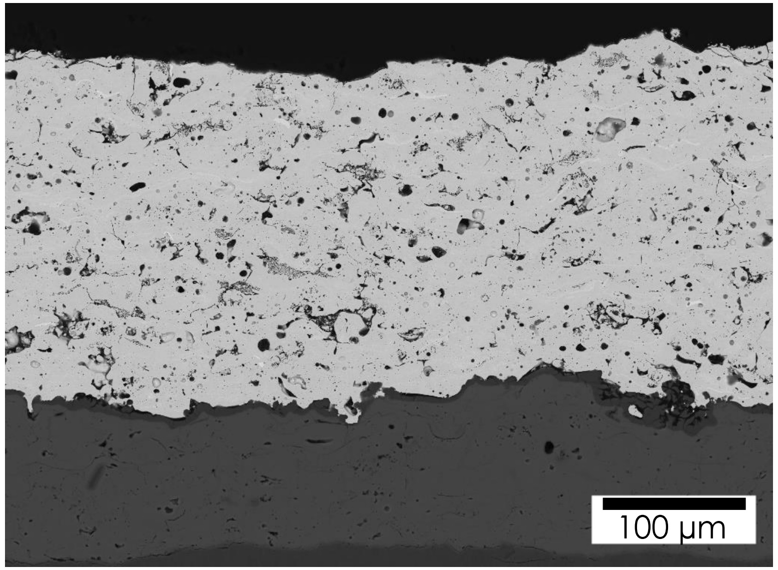
Doped EBCs show improvements at 1250°C, 100h exposure , 1-h steam cycling (2023)

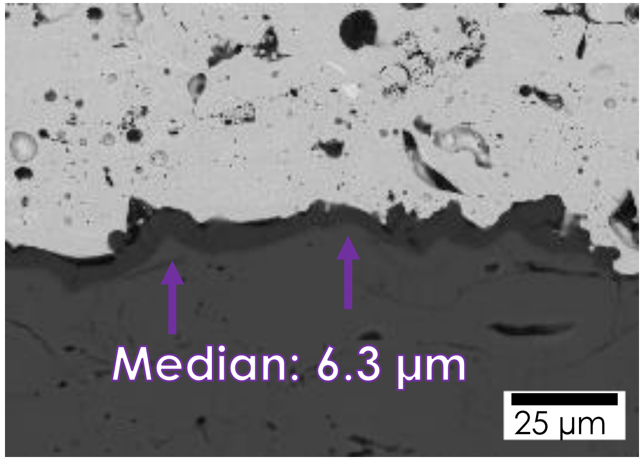
YbDS/YbMS (Stony Brook)



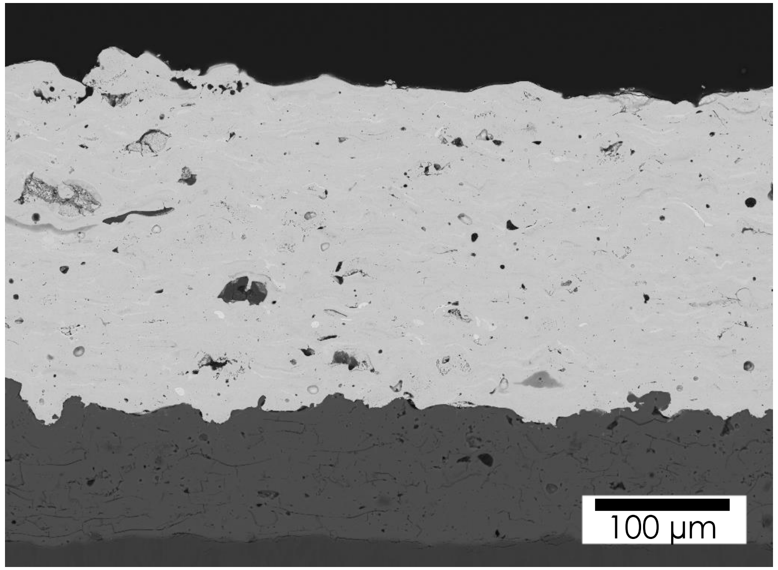


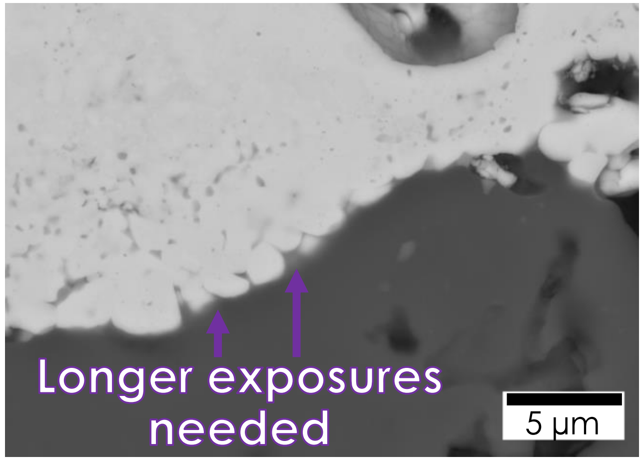
YbDS (NASA)



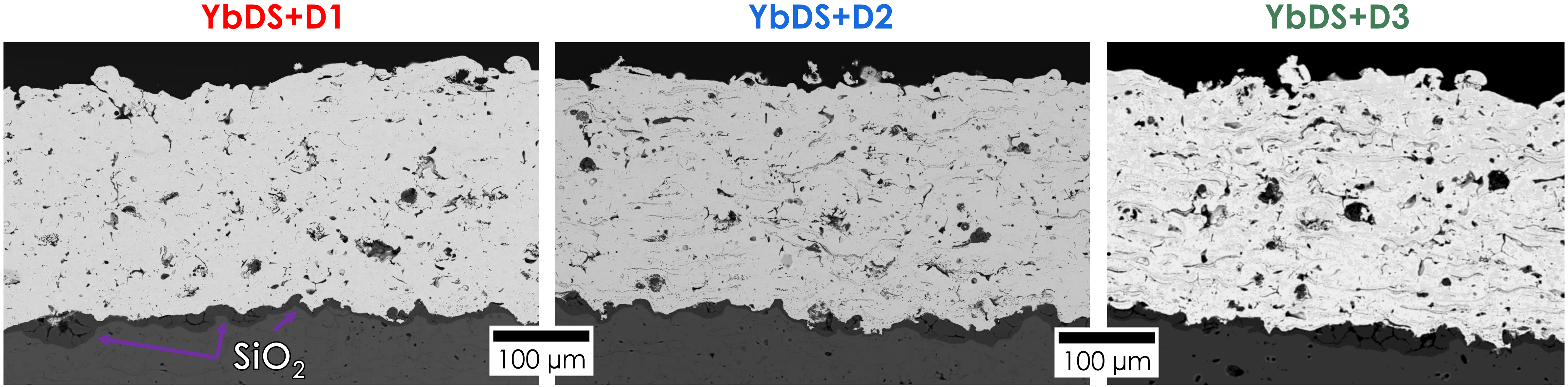


YbDS+D1 (NASA)

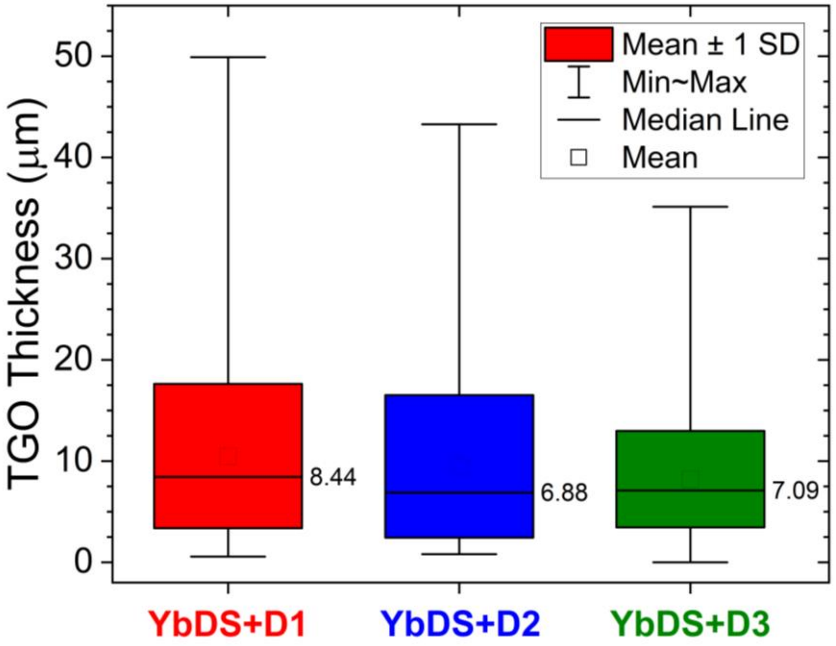




NASA doped EBCs show similar TGO thicknesses after 500h at 1350°C (2023)



- Similar global TGO thicknesses
- **14,000-21,000 measurements over ~3.5 mm cross-sections**
- Abnormal TGO growth greatest for **YbDS+D1** for 100, 300, 500h exposures
- Higher dopant concentration slightly decreases median TGO thickness



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https://github.com/TriplePointCat/SOFIA-CV

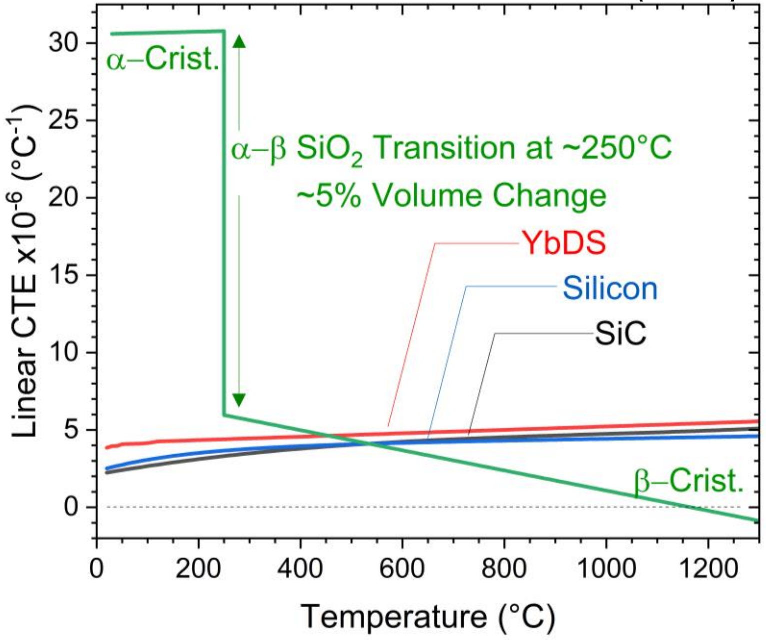
$$\sigma_{ox} = E_{ox}\,\Delta T\,\Delta\alpha$$

Causes for EBC delamination addressed in simple FEM

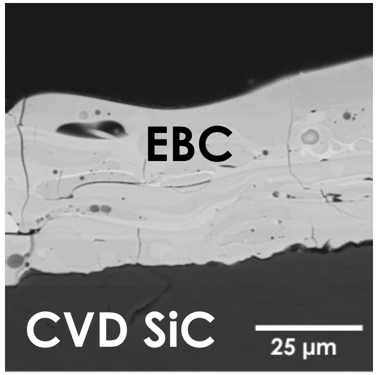
- Cooling from 1350°C to RT
- SiO_2 phase transformation at 250°C
  - 5% vol. change
- Temperature dependent CTE and Young's Modulus included for all layers

Cristobalite properties vary greatly →

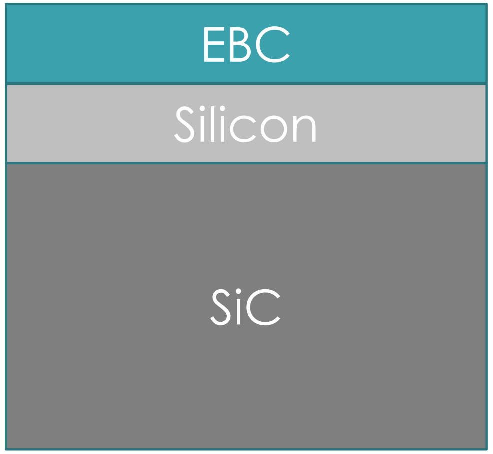
M. Lance et. al, ***JACerS*** *(2023).*

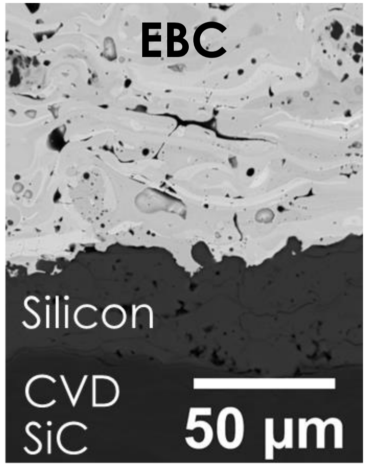


Model 1 (Theoretical)

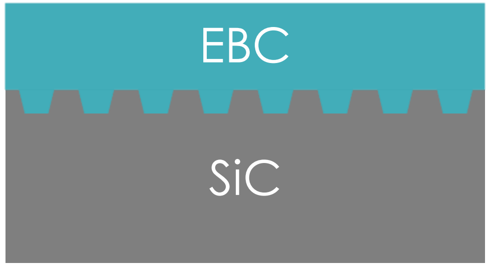


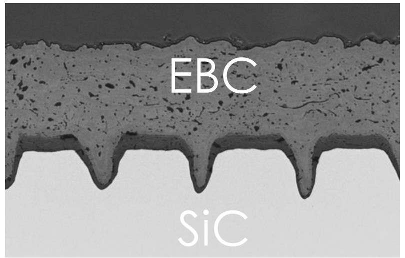
Model 2 (Research Standard EBC System)





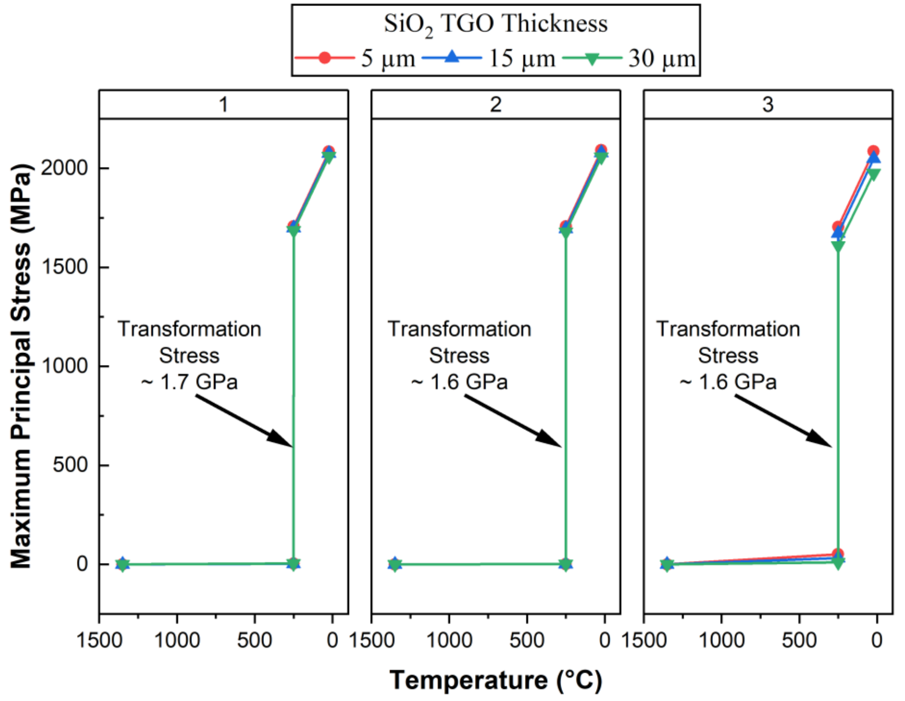
Model 3 (ORNL Si-free Trial Architecture)





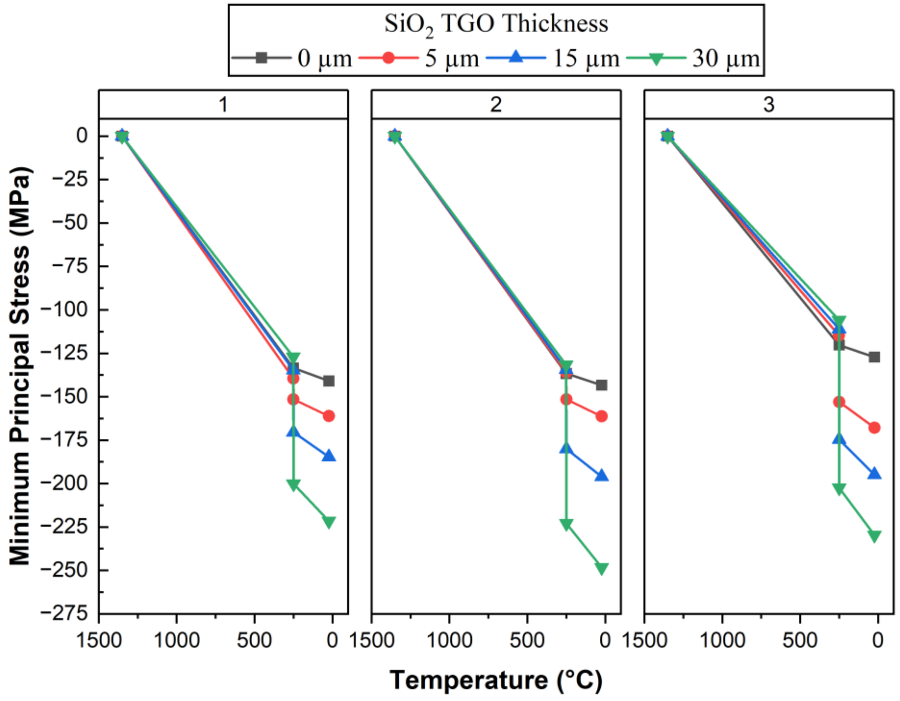
"Defect-free" 2D FEM initial results for each model (1, 2, 3)

SiO_2 TGO Stress on Cooling



- Phase transformation dominates all system stresses
- Overestimate, due to no pre-existing cracks in model

EBC Stress on Cooling



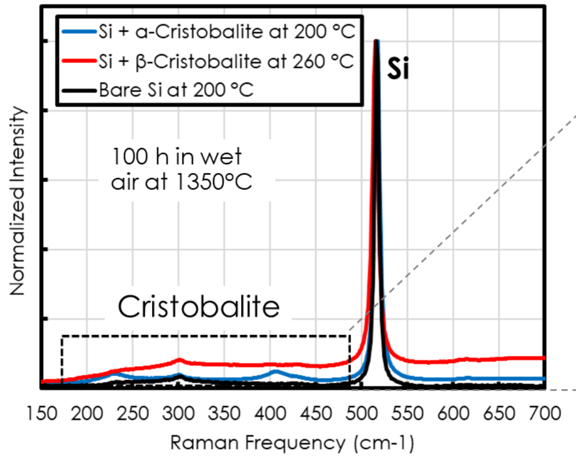
- EBC compressive stress increases with SiO_2 TGO thickness

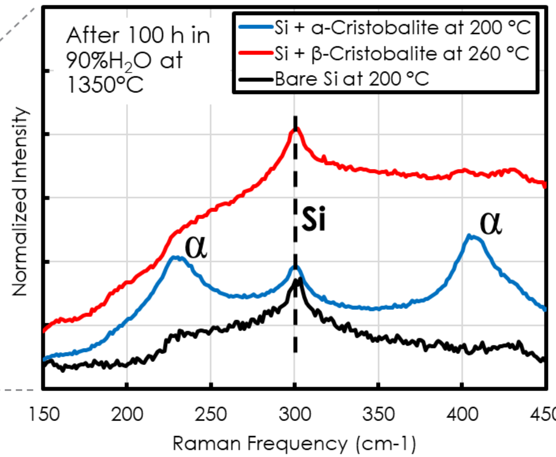
Now… Can we measure this experimentally?

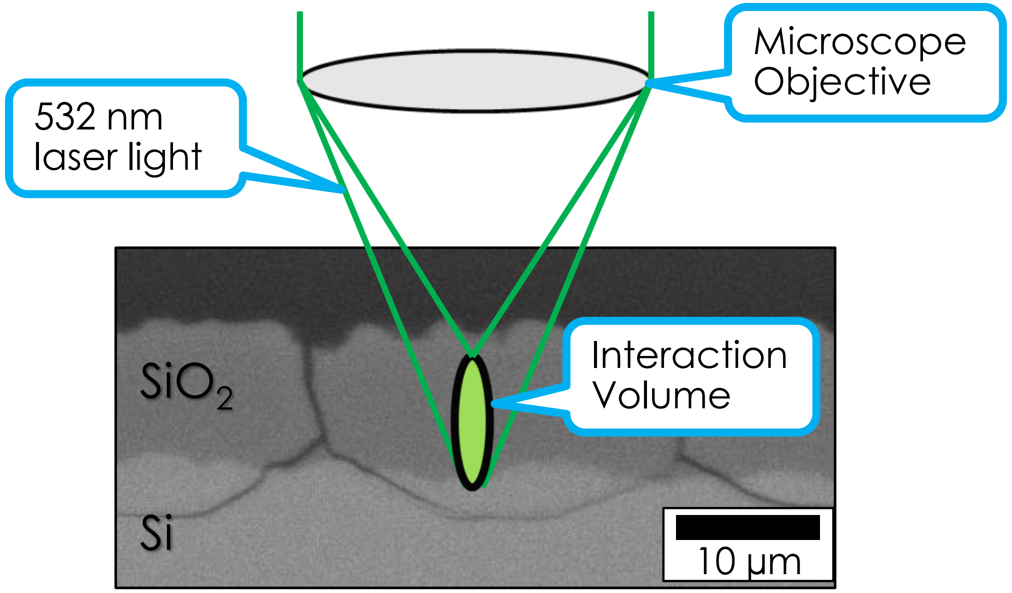
Aguirre, Lin, Ridley, Pint, ORNL internal review.

Renishaw Raman Microprobe allows for characterization of phase and stress evolution

- Raman Spectroscopy with heating stage attachment (600°C)
- 532 nm (green) laser, 50x lens, 2 µm spot size
- Peak shifts ∝ f(Temperature, Stress)
  - Calibrations performed for Si







*M. Lance et. al, **JACerS** (2023).*

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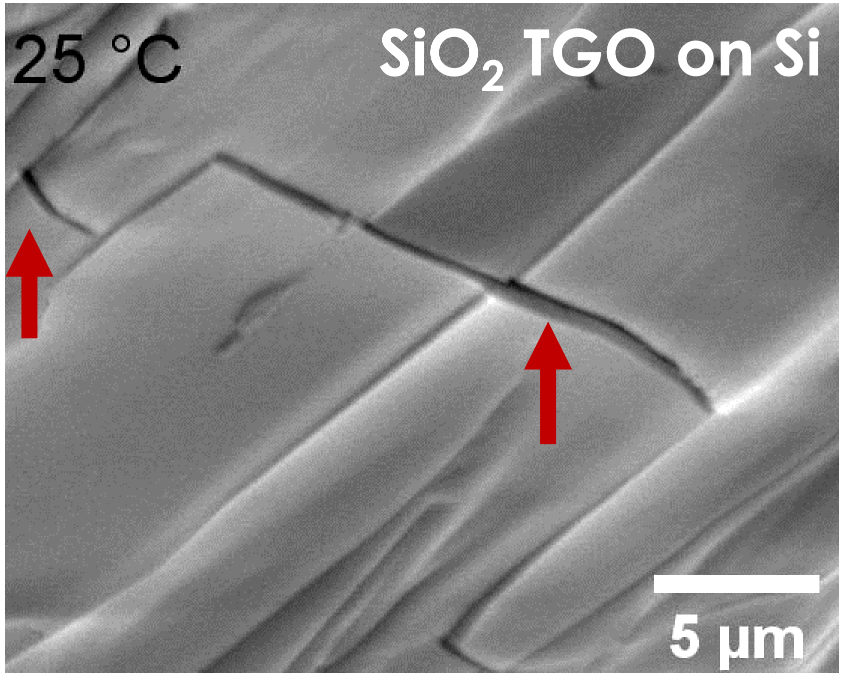
Visualized cristobalite (SiO_2) phase transformation with SEM and measured stress with Raman without EBC

SEM Heater Stage

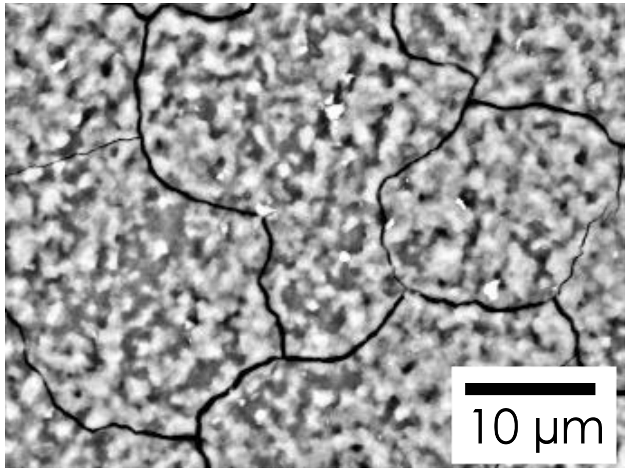
SiO_2 crack closure at phase change

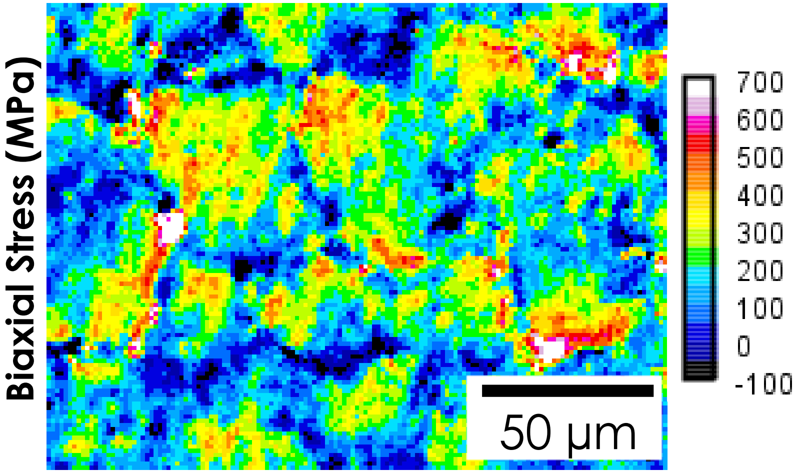
**Specimen tilted 70°*



High-temp. Raman Spectroscopy

300 – 500 MPa increase from phase change



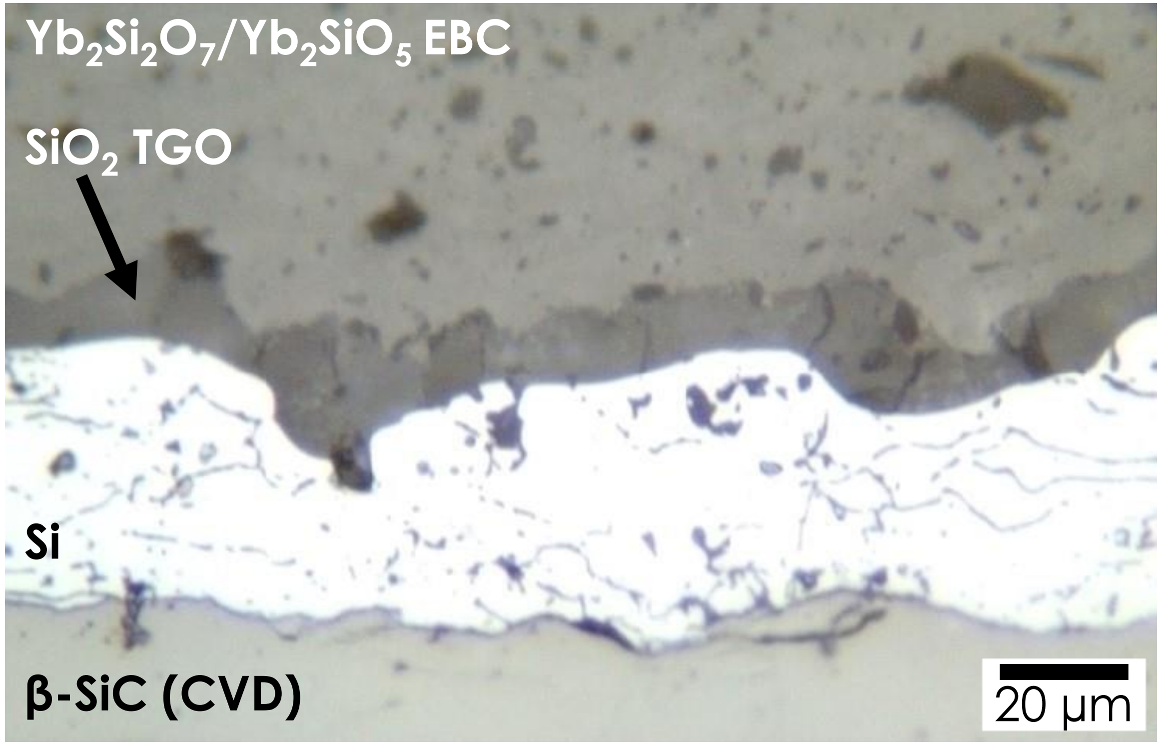


M. Lance et. al, ***JACerS*** (2023).

CTE difference & ~5% volume change cause cracking, but what happens when EBC is applied?

Raman Stress and phase measurements on a full EBC system in cross-section at elevated temperatures was attempted

Light Optical Image



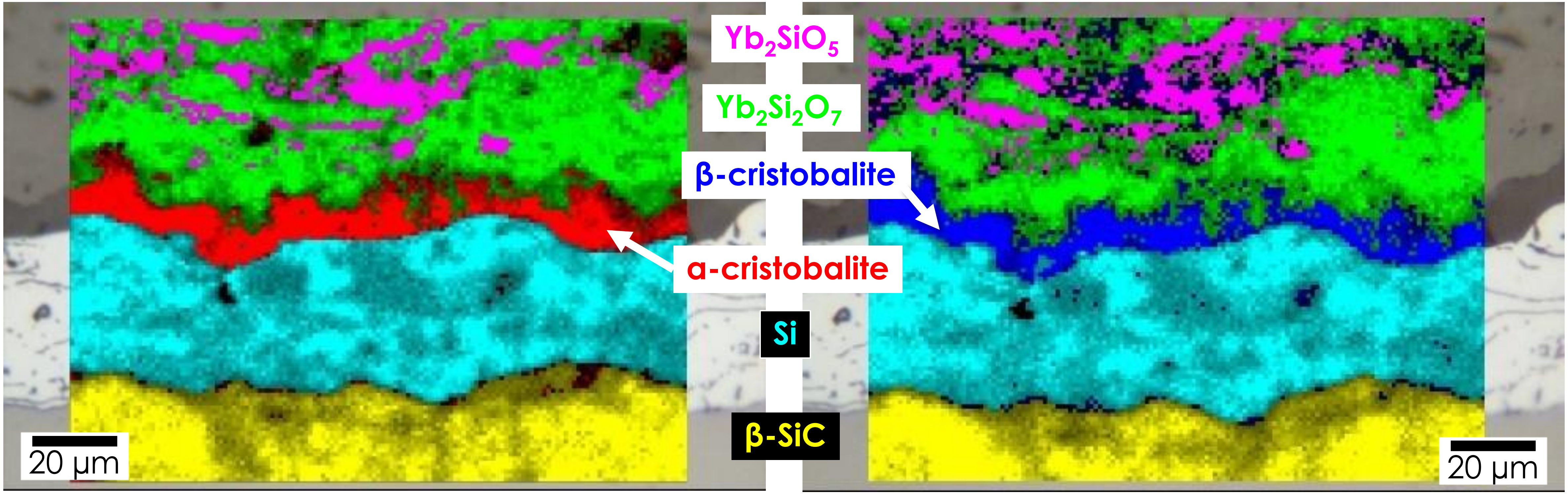
1000 h (10-100h cycles) at 1350 °C in wet air

ORNL EBC made by Stony Brook University

- The sample was mounted in epoxy, polished and then removed from the epoxy prior to heating from 220 to 290 °C

Methodology developed for high-temperature Raman in cross-section after EBC exposure to cyclic steam

260°C, a-cristobalite TGO | 270°C, β-cristobalite TGO

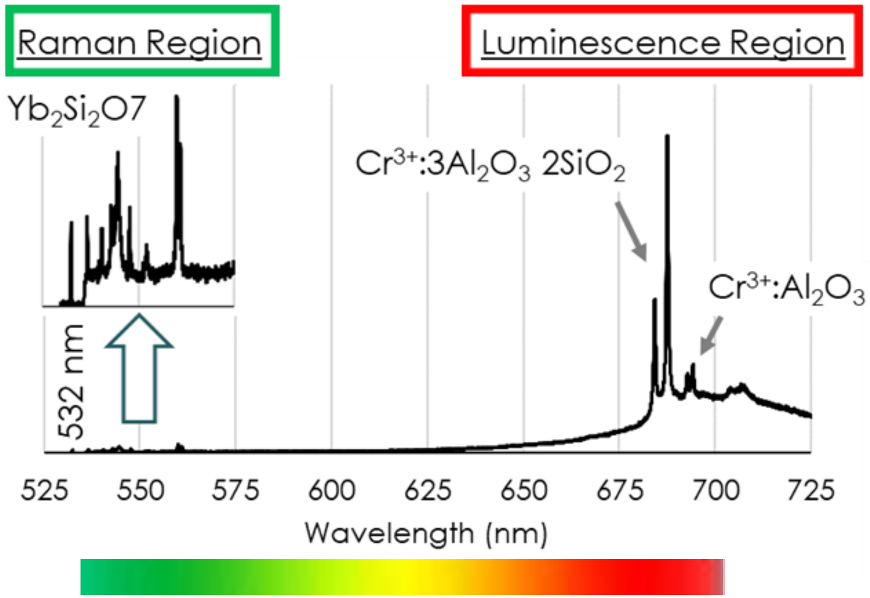


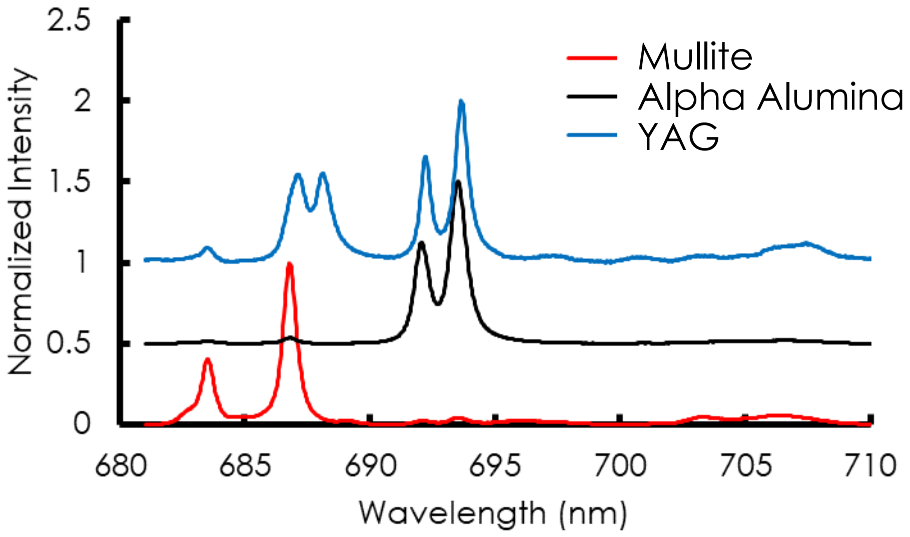
- Phase maps created from Raman Spectra with principle component analysis
- a-cristobalite phase disappears after 260°C due to phase transition

Goal: Quantify thermal and phase transformation stresses with EBC

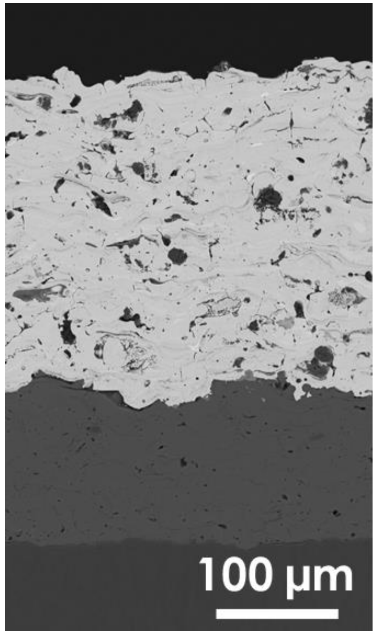
Stress measurements in doped EBCs
Photo-Stimulated Luminescence Spectroscopy (PSLS)

$Yb_2Si_2O_7$ EBC modified with Mullite ($3Al_2O_3$ $2SiO_2$) and YAG ($Y_3Al_5O_{12}$)





YbDS+D3

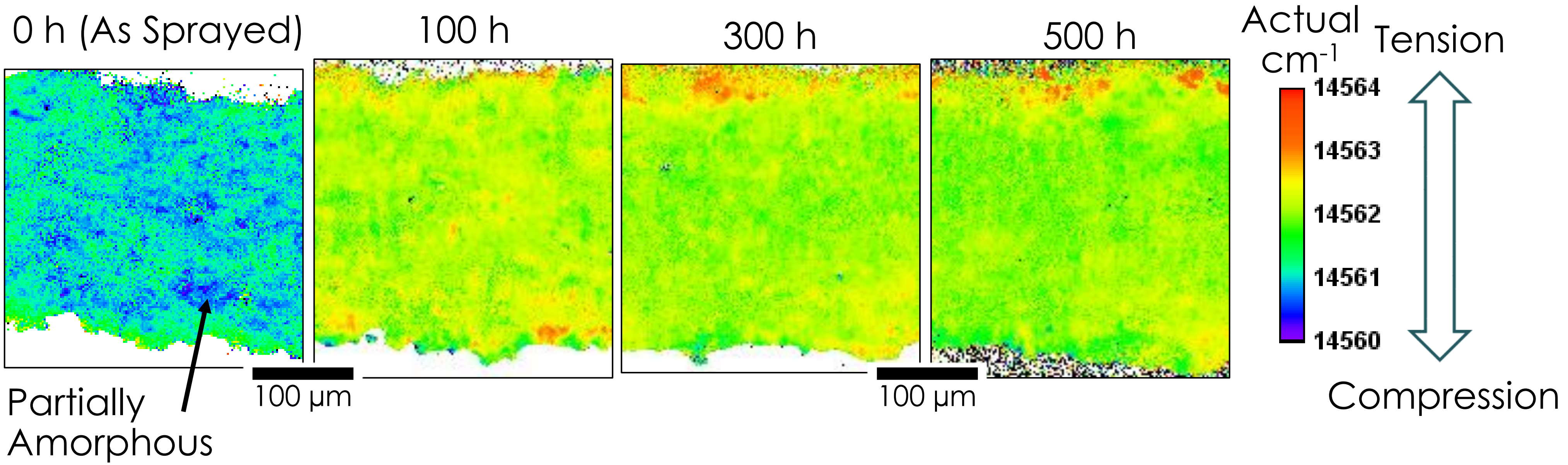


- Raman microprobe used for PSLS spectra acquisition
- Trace Cr^{3+} (few ppm or less!) substitutes for Al and can absorb green light and emit R(Red)-lines

EBC Stress Measurement using Photo-stimulated luminescence spectroscopy of Mullite: Thermal & TGO growth stresses

YbDS+D3, doped EBC (NASA)

1-h cycles at 1350°C in wet air



- R-lines shift 7.6 cm^{-1}/GPa (Lipkin and Clarke, 1996)
- Crystallized EBC before steam exposure needed for baseline*
- Average minor compression in EBC, tensile near EBC-gas surface

Dopants can allow for NDE of EBC stresses in service

EBC Stress Measurement using Photo-stimulated luminescence spectroscopy of Mullite: Thermal & TGO growth stresses

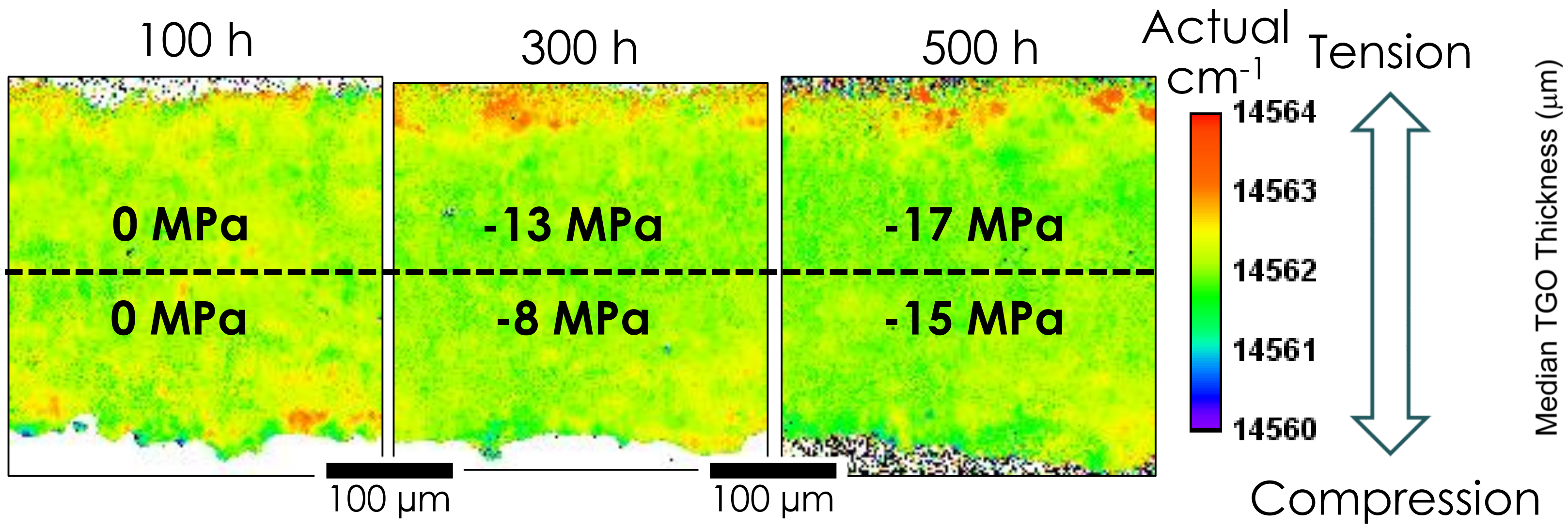
YbDS+D3, doped EBC (NASA)
1-h cycles at 1350°C in wet air

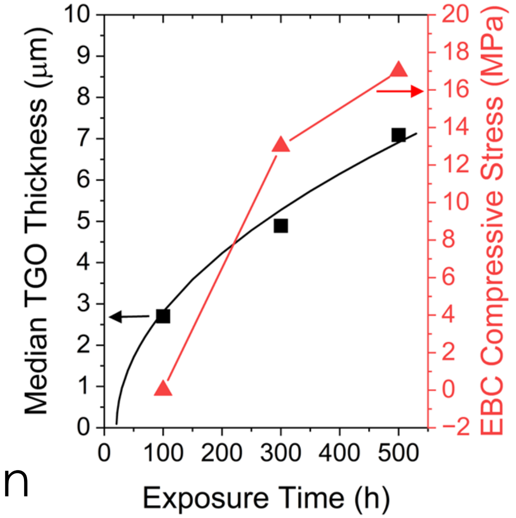
Parabolic EBC stress change

Average EBC Stress

Measured:

2D FEM:





- 100h test sample set as zero stress reference to visualize general trend
- Average EBC stress agrees with simplified 2D model results

EBC stress changes as a function of SiO_2 thickness

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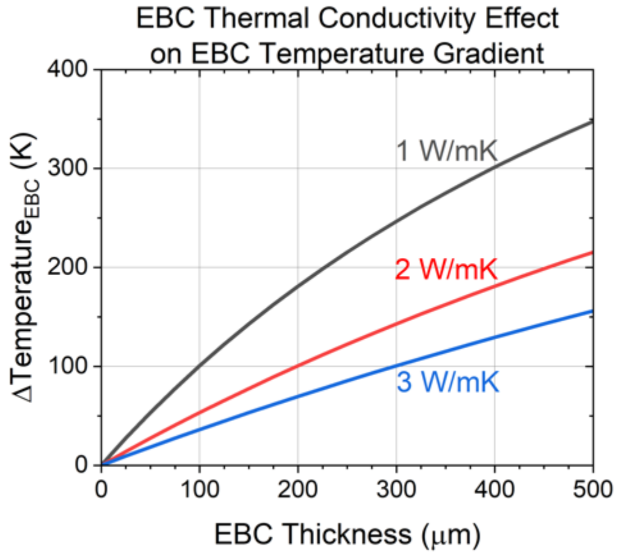
Clear directions going forward

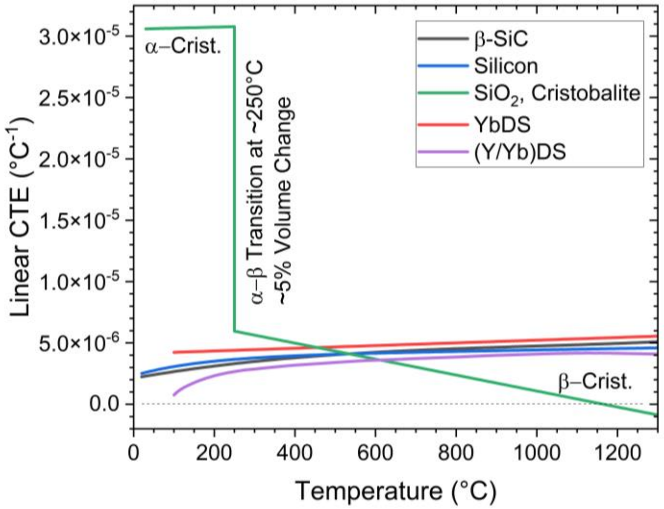
1. We need better EBCs

- Thermal & oxidant barrier
- *Need replacement for Si bond coating (T_{melt} = 1414°C)*
- *Understand effects of dopants on oxidation*



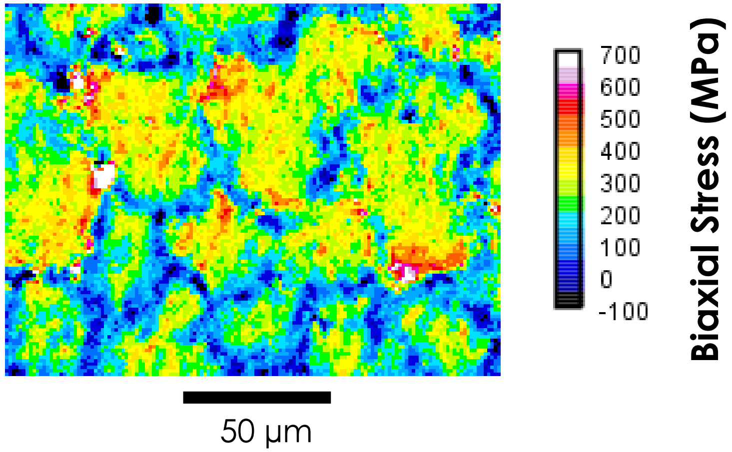
2. Understand/mitigate the SiO_2 phase trans-formation

- Need basic SiO_2 data
- *Stress impact on EBC needed for lifetime model*



3. Characterization to further understanding

- EBC stress evolution with steam cycling
- *Microstructure-relevant modelling for guidance/comparisons*



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Thank you for your attention!
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1. Ridley M, Garcia E, Kane K, Sampath S, Pint B. Environmental barrier coatings on enhanced roughness SiC: Effect of plasma spraying conditions on properties and performance. **Journal of the European Ceramic Society**. 2023;43(14):6473–6481.
2. Lance M, Ridley M, Kane K, Pint B. Raman spectroscopic characterization of SiO2 phase transformation and Si substrate stress relevant to EBC performance. **Journal of the American Ceramic Society**. 2023; 106: 6205–6210.
3. Ridley M, Kane K, Lance M, Parker C, Su Y.-F., Sampath S, Garcia E, Sweet M, O'Connor M, Pint B, "Steam Oxidation and Microstructural Evolution of Rare Earth Silicate Environmental Barrier Coatings," **Journal of the American Ceramic Society** (2022).
4. Stack P, Kane K, Sweet M, Parker C, Lance M, Ridley M, Pint B, "Dry air cyclic oxidation of mixed Yb/Y disilicate environmental barrier coatings and bare silica formers," **Journal of the European Ceramic Society** 42 (2022) 3345-3350.
5. Pint B, Stack P, Kane K, "Predicting EBC Temperature Limits for Industrial Gas Turbines" ASME Paper #GT2021-59408, for Turbo Expo 2021 Virtual Conference and Exhibition, June 11-15, 2021 & **Diesel and Gas Turbine Worldwide** Jan.-Mar. issue (2022) p.40-43.
6. Kane K, Garcia E, Stack P, Lance M, Parker C, Sampath S, Pint B, "Evaluating steam oxidation kinetics of environmental barrier coatings," **Journal of the American Ceramic Society**, 105 (2022) 590-605.
7. Kane K, Garcia E, Lance M, Parker C, Sampath S, Pint B, "Accelerated oxidation during long-term cycling of ytterbium silicate environmental barrier coatings at 1350°C," **Journal of the American Ceramic Society**, 105 (2022) 2754-2763.
8. Kane K, Garcia E, Stack P, et al. Evaluating steam oxidation kinetics of environmental barrier coatings. **Journal of the American Ceramic Society**. 2022;105(1):590–605.
9. Kane K, Garcia-Granados E, Uwanyuze R, Lance M, Unocic K, Sampath S, Pint B, "Steam oxidation of atmospheric plasma sprayed ytterbium disilicate environmental barrier coatings with and without a silicon bond coat," **Journal of the American Ceramic Society** 104 (2021) 2285-2300.
10. Kane K, Stack P, Schappel D, et al. Oxidation of 3D-printed SiC in air and steam environments. **Journal of the American Ceramic Society**. 2021;104(5):2225–2237.
11. Kane K, Garcia E, Uwanyuze S, et al. Steam oxidation of ytterbium disilicate environmental barrier coatings with and without a silicon bond coat. **Journal of the American Ceramic Society**. 2021;104(5):2285–2300.
12. Su Y.-F., Stack P, Stephens C, et al. Quantifying High Temperature Corrosion. **OnePetro**; 2021.