Hafnia-Based Thermal Barrier Coatings for Advanced Hydrogen Turbine Technology

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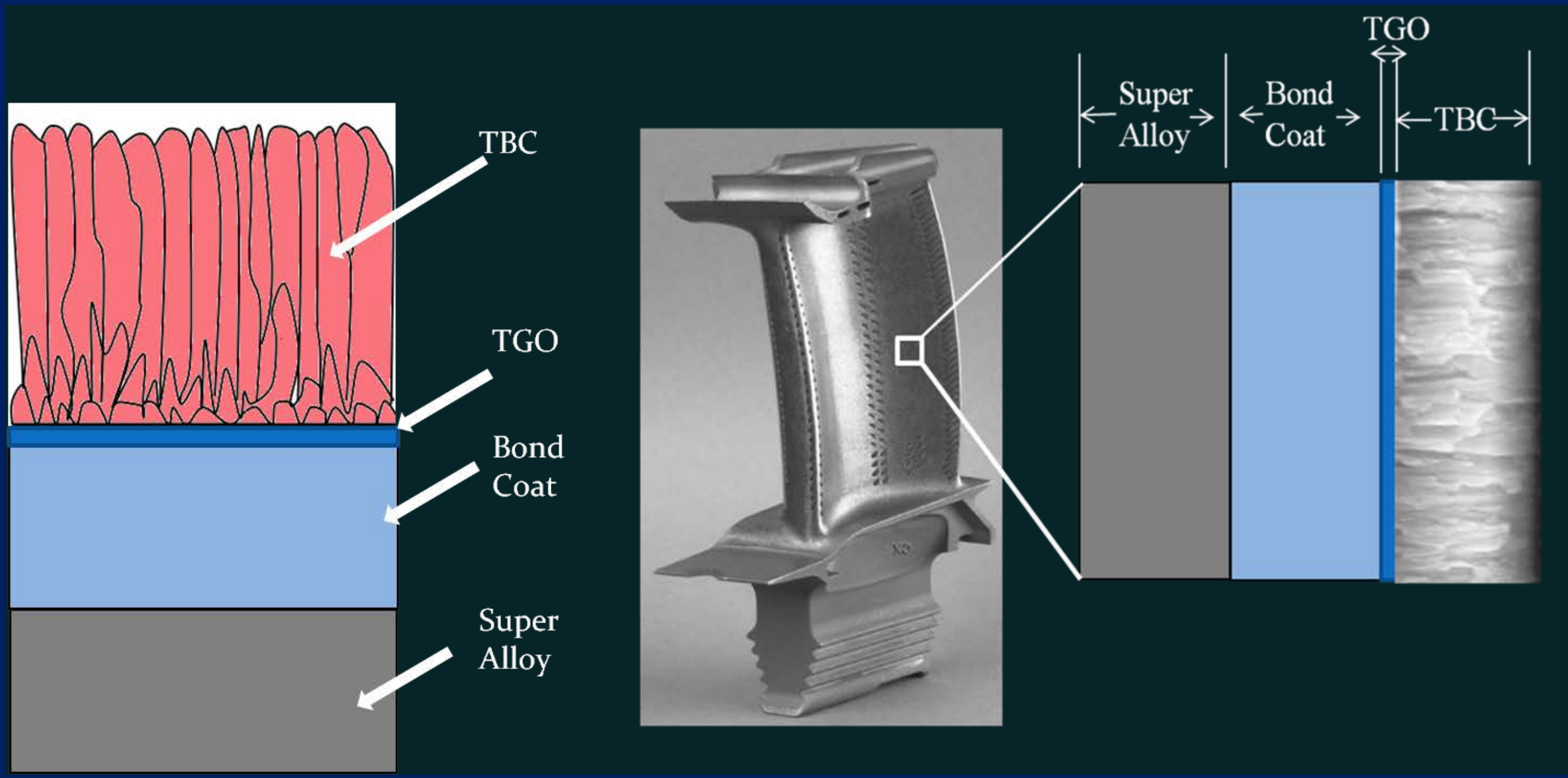
Agenda

- Introduction
- Experiments
  - ► Synthesis
  - ► Characterization
  - ► Hot gas exposure
- Results
  - ► Y_2O_3-HfO_2 (YSH)
  - ► Y_2O_3-HfO_2-ZrO_2(YSHZ)
  - ► Gd_2O_3-HfO_2 (GSH)
- Conclusions

TBCs

- Multifunctional thick coatings of low thermal conductivity ceramic material
- Protect the metal component from extreme temperature
- Allow to increase the turbine operating temperature
- Increase the efficiency

Evans et al., *Prog. Mater. Sci.* 46, 505 (2001);
Nitin et al., *Science* 296, 280 (2002);
D.R. Clarke, S.R. Phillpot, *Mater. Today* 8, 22 (2005)


TBC
TGO
Bond Coat
Super Alloy
TGO
Super Alloy
Bond Coat
TBC

TBCs

Current Standard: YSZ (Yttria Stabilized Zirconia)

Mainly due to ZrO_2: refractory oxide, ‘coatings’ using well-known PVD technology, and mechanical stability and low thermal conductivity

Y_2O_3: stabilizer

YSZ Problems: Temperature Tolerance (1200 ^{o}C) and Durability (cracking and spallation due to phase and, hence, volume change)

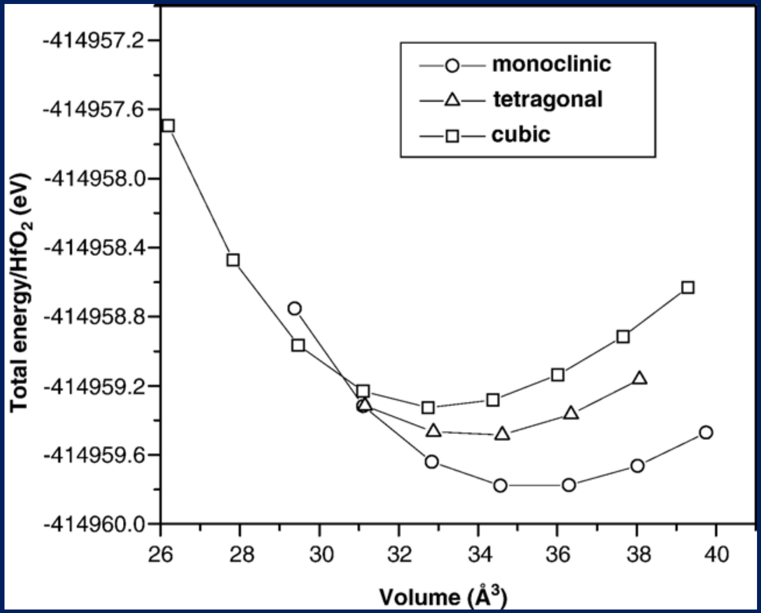
Goal (Ref: DE-FOA-0000031):

Temperature Tolerance $\geq$ 1300 ^{o}C

Hafnia-Based TBCs

HfO$_2$ exhibits:

- Higher melting point (2900 ºC)
- Lower thermal conductivity
- Crystal structure and phase transformation behavior



m-HfO$_2$

1700 ºC

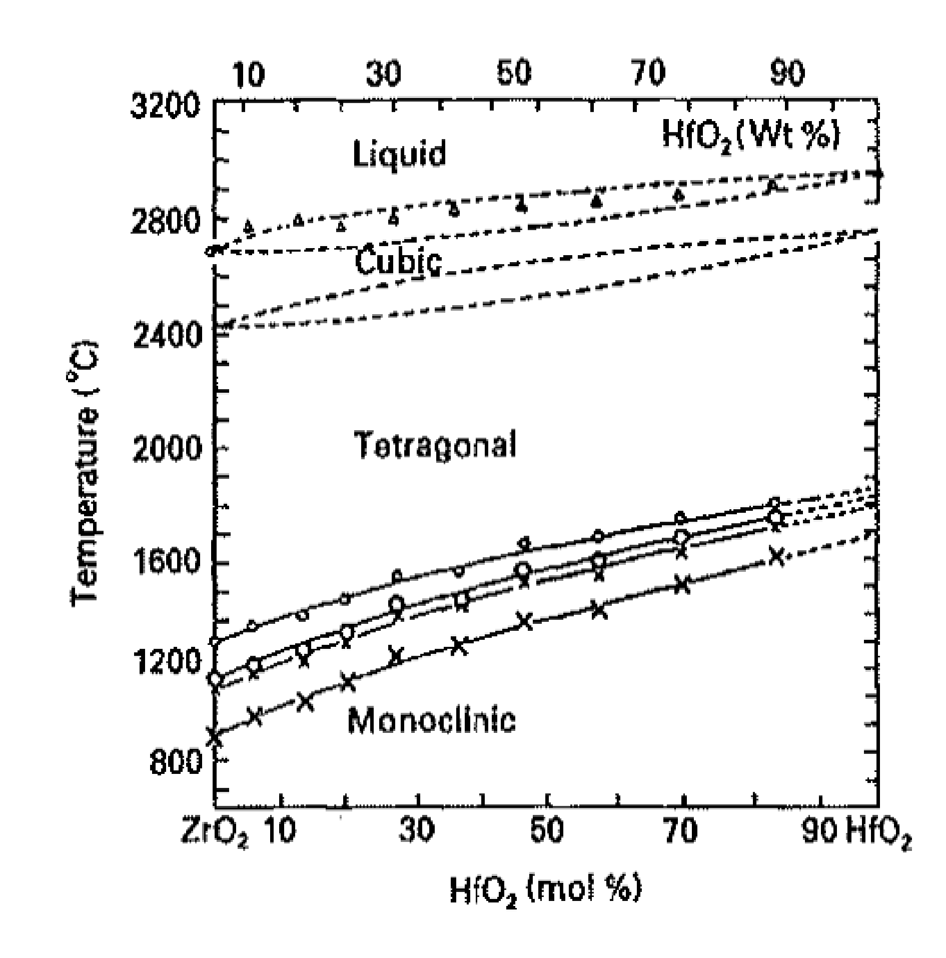
t-HfO$_2$

2700 ºC

c-HfO$_2$

(2900 ºC)

Hafnia-Zirconia Phase Diagram



R. Ruh, H. J. Garrett and R. F. Domagala, *J. Amer. Ceram. Soc. 51* (1968) 23

- These ceramics are miscible in all proportions and at all temperatures

Hafnia-Zirconia Phase Diagram

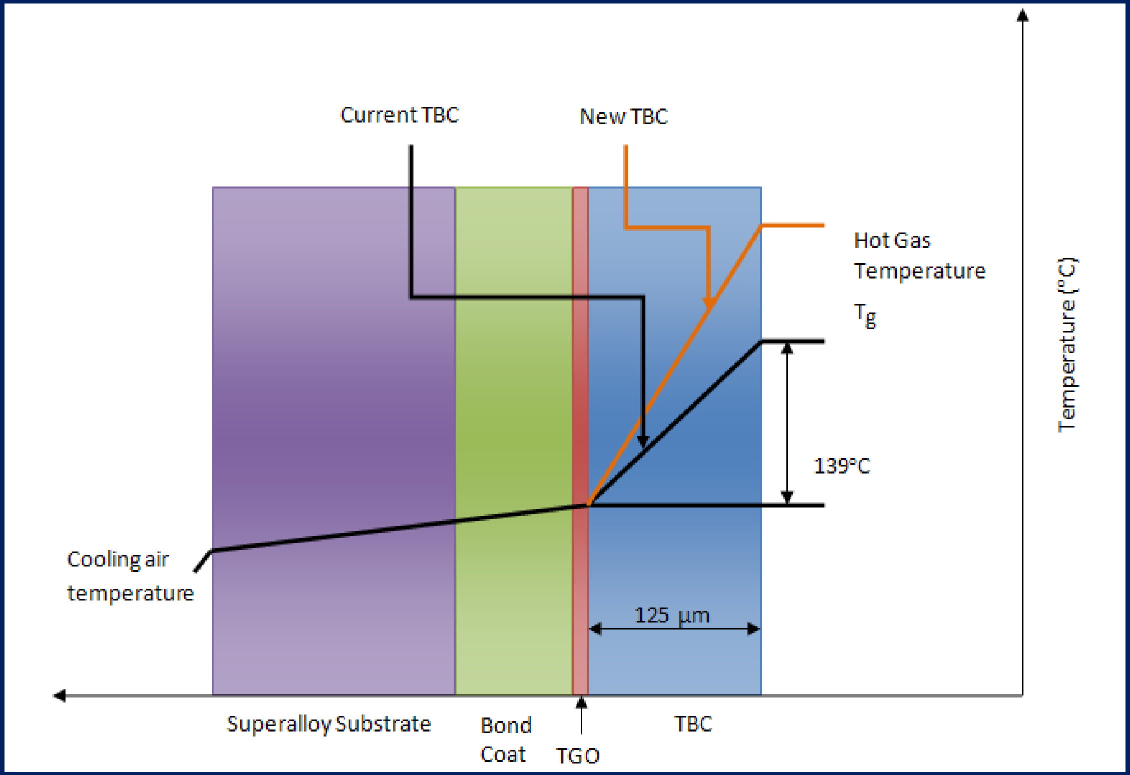
► The phase transformation temperature is several hundred degrees higher than that for ZrO_2

► The difference between the heating transformation (m-t) temperature and the cooling transformation (t-m) temperature is smaller than that which occurs in ZrO_2, i.e. the temperature hysteresis effect in HfO_2 is less pronounced than that in ZrO_2

► The established density change associated with the transformation in HfO_2 is much smaller than that in ZrO_2 which implies that the volume expansion and shear strain associated with the transformation in the former are smaller than those in the latter

Wang et al., *J. Mater. Sci. 27* (1992) 5397

Thermal Conductivity Reduction



Heat flux across area A:

$$\frac{dQ}{dt} = -KA\frac{dT}{dx}$$

K: thermal conductivity

dT/dx: temp. gradient

$$\Delta T = \left(\frac{1}{KA}\right)\Delta x\left(\frac{dQ}{dt}\right)$$

Objectives

- Design and fabrication of hafnia-based coatings
- Characterization and evaluation of the coatings
- Look for:
  - Higher temperature tolerance
  - Lower thermal conductivity
  - Higher materials' strength
  - Enhanced durability

EXPERIMENTS

Materials

TBC Candidates:

Y_2O_3 stabilized HfO_2 (YSH)

Y_2O_3 stabilized $ZrO_2 – HfO_2$ (YSHZ)

($ZrO_2 – HfO_2$ Mixed Composition)

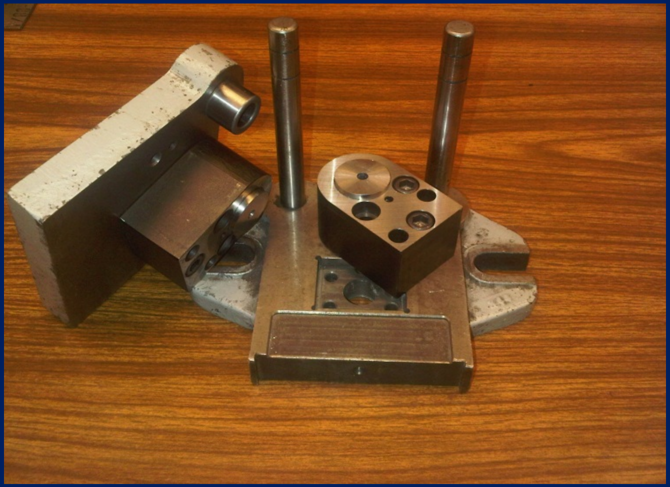
$Gd_2O_3 – HfO_2$ (GSH)

Substrate(s):

- Ni super alloy(IN-738)
- SS-403
- Alumina

Target/Ingot Preparation

Tineous Olsen/Die Press



<u>Targets/Ingots</u>:

(1) YSH
(2) YSHZ (variable composition)
(3) GSH (variable composition)

YSH and YSHZ Composition

YSH: 7.5 % Y_2O_3: HfO_2

YSHZ

YSHZ-1 : (HfO_2 : ZrO_2 = 4:1)

YSHZ-2 : (HfO_2 : ZrO_2 = 2:1)

YSHZ-3 : (HfO_2 : ZrO_2 = 1:2)

YSHZ-4 : (HfO_2 : ZrO_2 = 1:4)

YSHZ-5 : (HfO_2 : ZrO_2 = 1:1)

GSH Composition

Gd_2O_3 = 0-40 mol%

Gd_2O_3 : 4 mol%
Gd_2O_3 : 8 mol%
Gd_2O_3 : 12 mol%
Gd_2O_3 : 20 mol%
Gd_2O_3 : 38 mol%

$\left.\begin{array}{l} Gd_2O_3 : 4 \text{ mol\%} \\ Gd_2O_3 : 8 \text{ mol\%} \\ Gd_2O_3 : 12 \text{ mol\%} \\ Gd_2O_3 : 20 \text{ mol\%} \\ Gd_2O_3 : 38 \text{ mol\%} \end{array}\right\}$ Balance HfO_2

Fabrication of TBCs and BC

PVD:

Sputtering

E-beam

<u>BC (MCrAlY; M=Co/Ni)):</u>

E-beam

APS

Target Synthesis

Precision balance

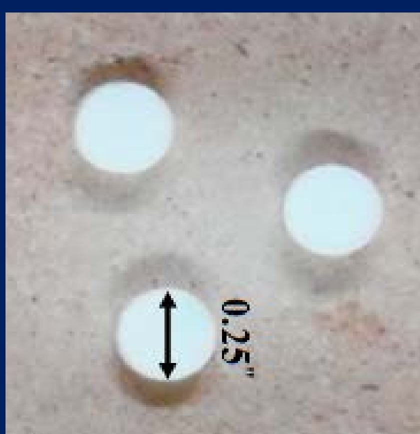
Mortar

Die and punch

Hydraulic compressor

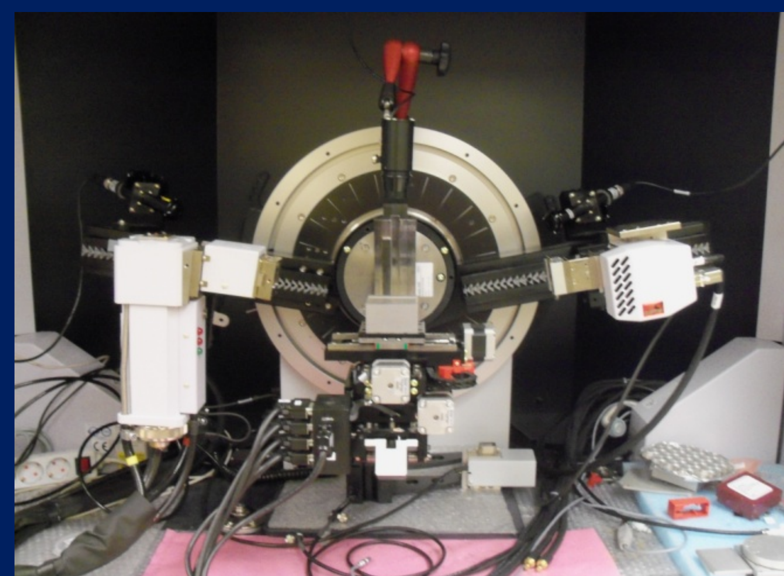
Target

Furnace



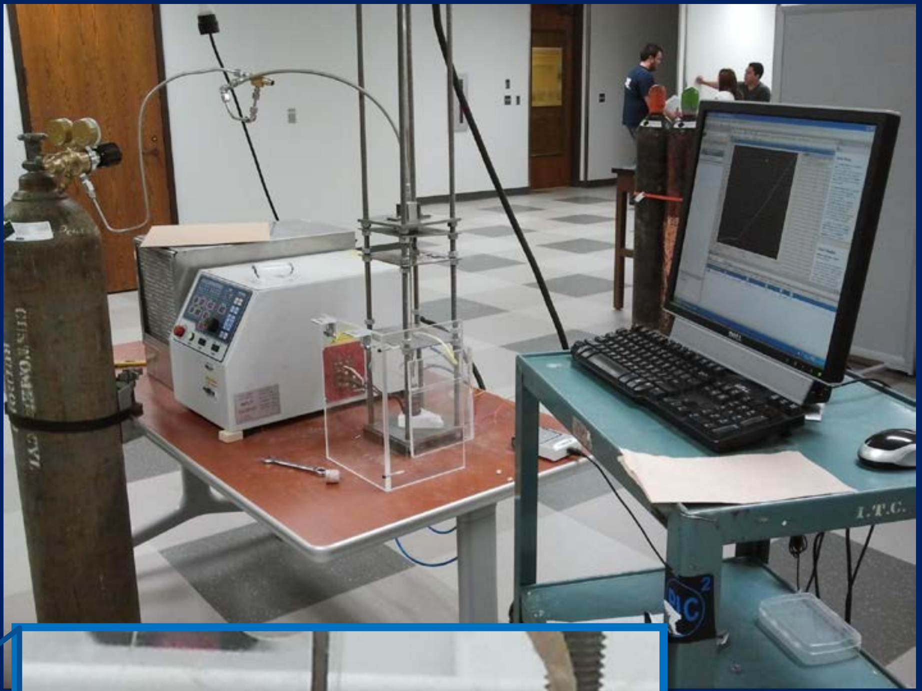
Characterization

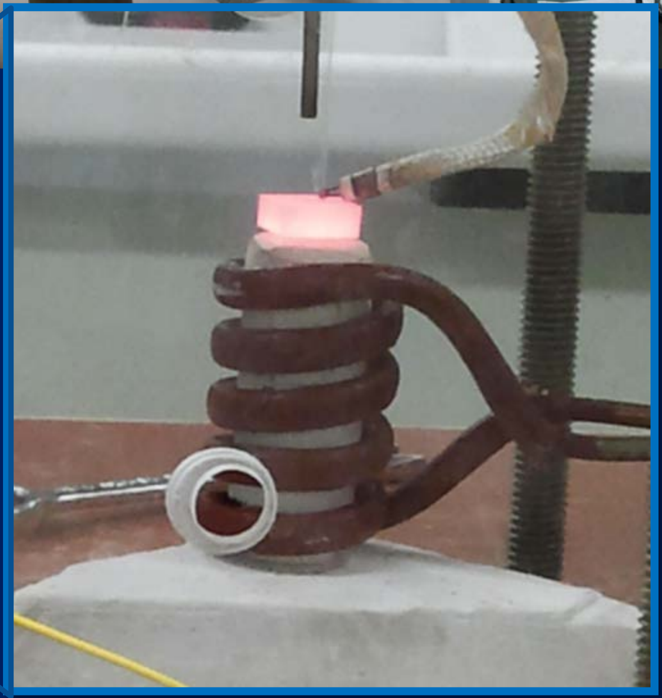
- XRD
- SEM
- EDS
- Laser 3D Microscope



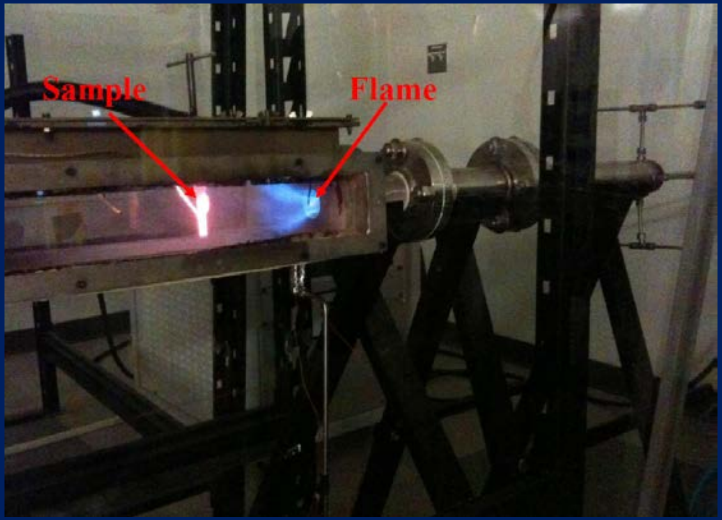
Thermal Cycling

Impact Test Apparatus





Hot Gas Exposure



Hot Gas Experiments

Experimental parameters:

Variable gas content: CH_4 to air ratio

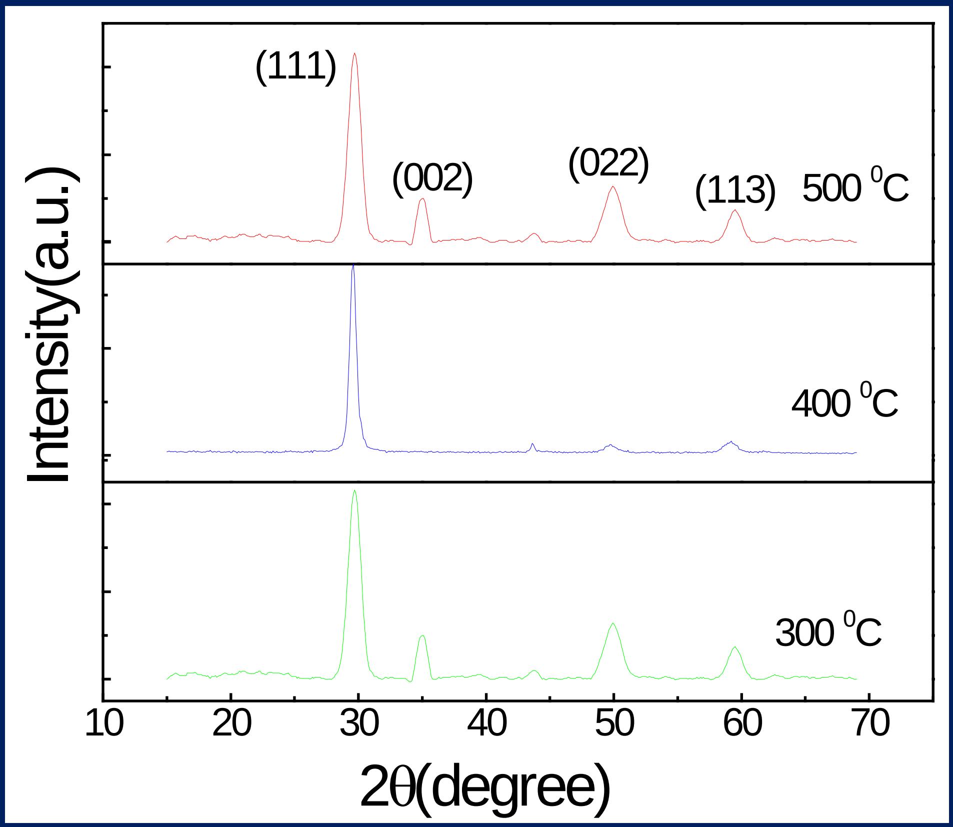
Gas impingement angle (0 and 90^o)

Variable exposure time

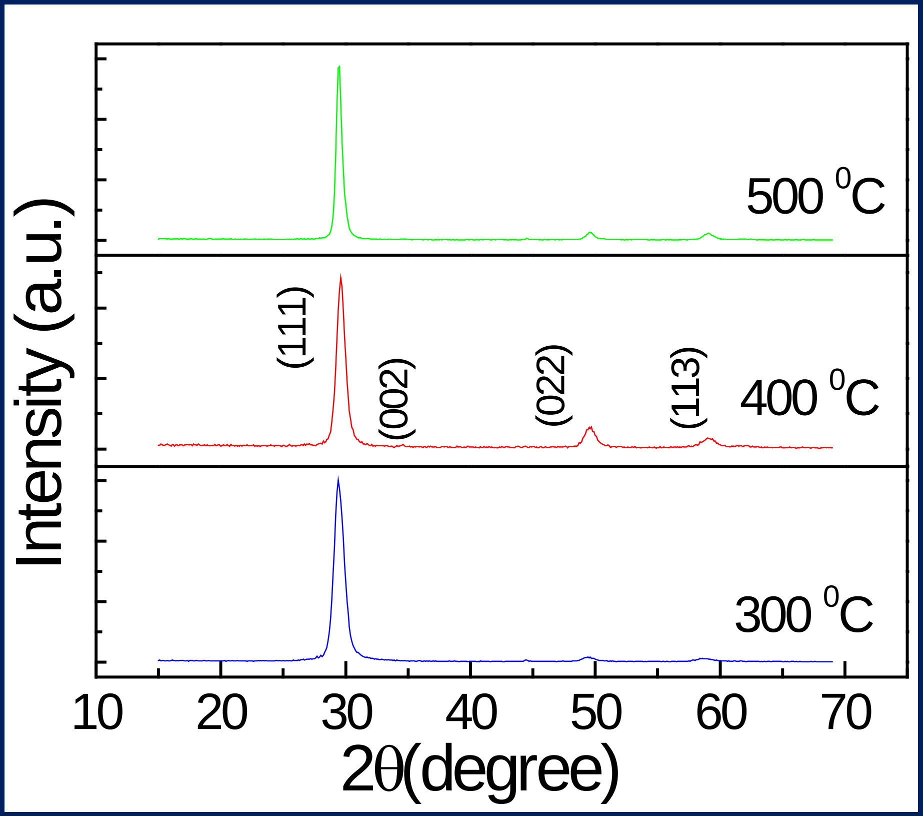
RESULTS

Structure and Phase Analysis - YSH

XRD patterns of YSH coatings on Inconel-738



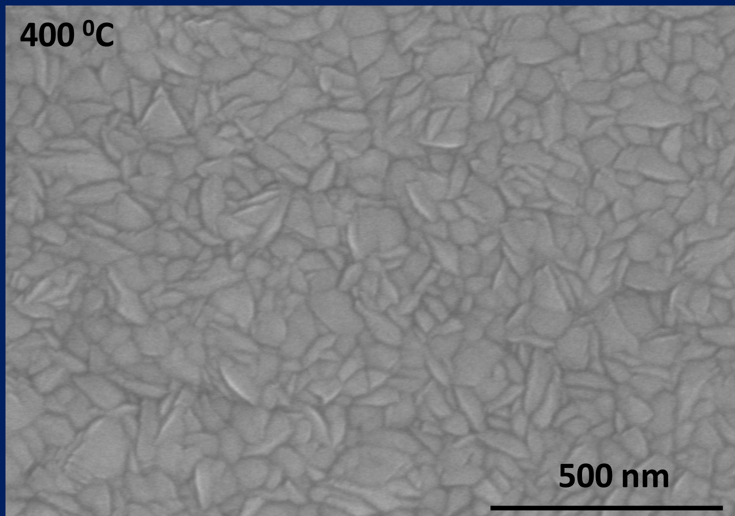
XRD patterns of YSH coatings on SS-403

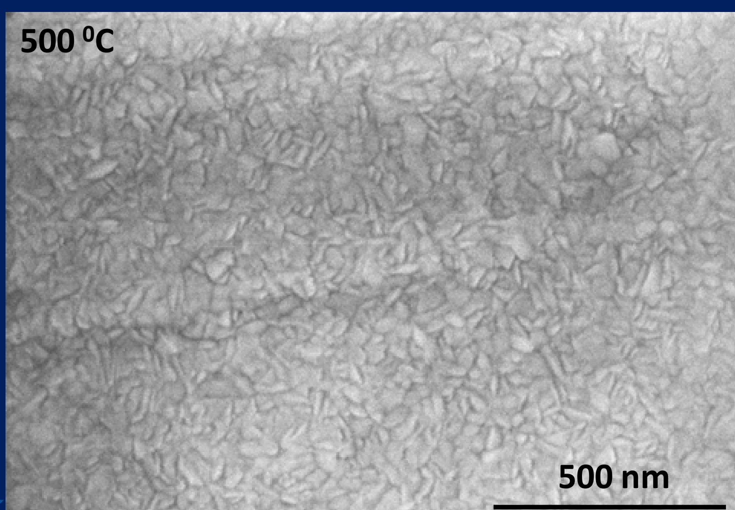


M. Noor-A-Alam et al., ASME JNEM (2012), In Press

Morphology and Chemistry – YSH Coatings

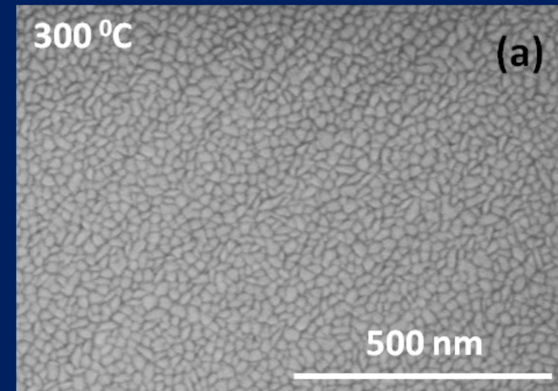
YSH on SS-403

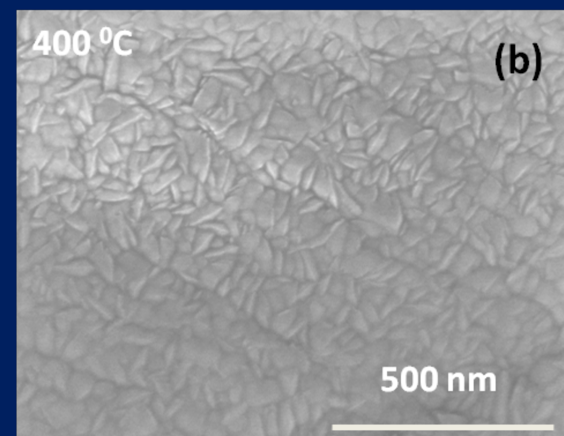


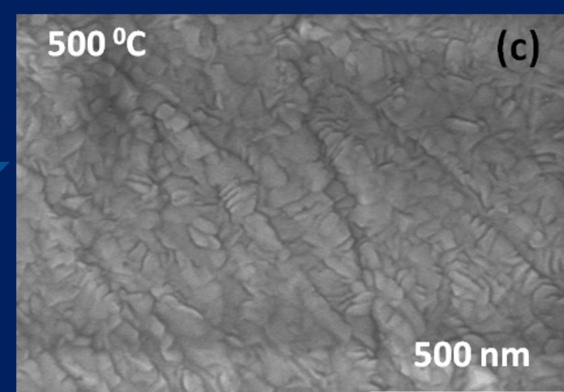


M. Noor-A-Alam and C.V. Ramana, *Ceram. Inter.* 38 (2012) 2957–2961

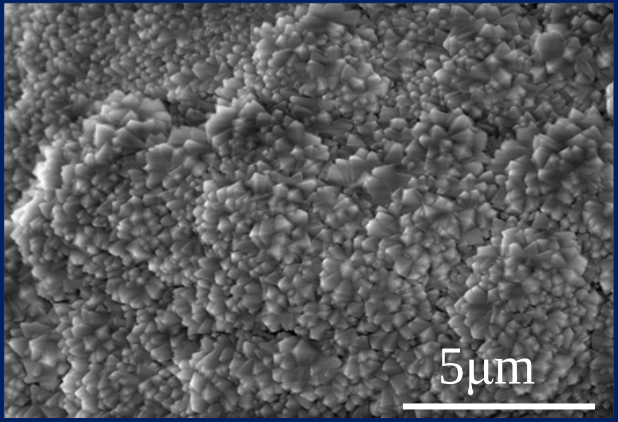
YSH on IN738

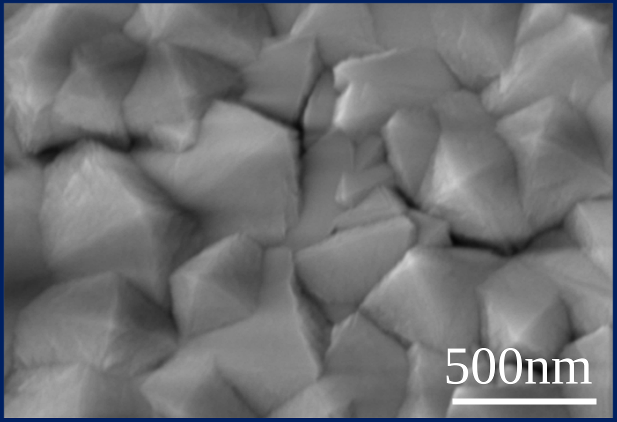




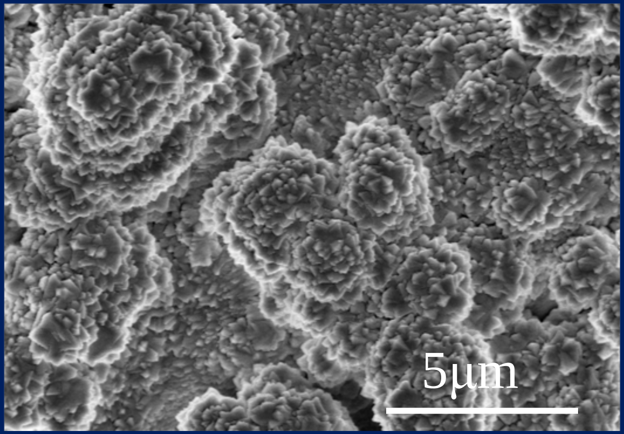


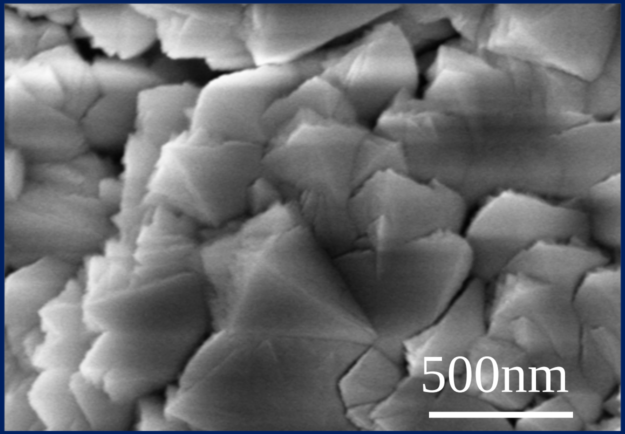
Morphology – YSH Coatings



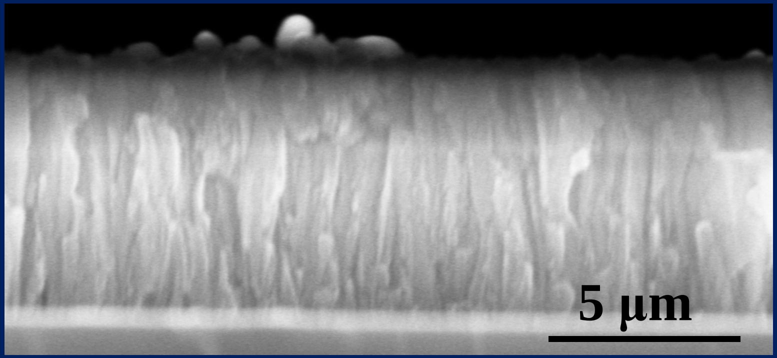


YHS on SS-403



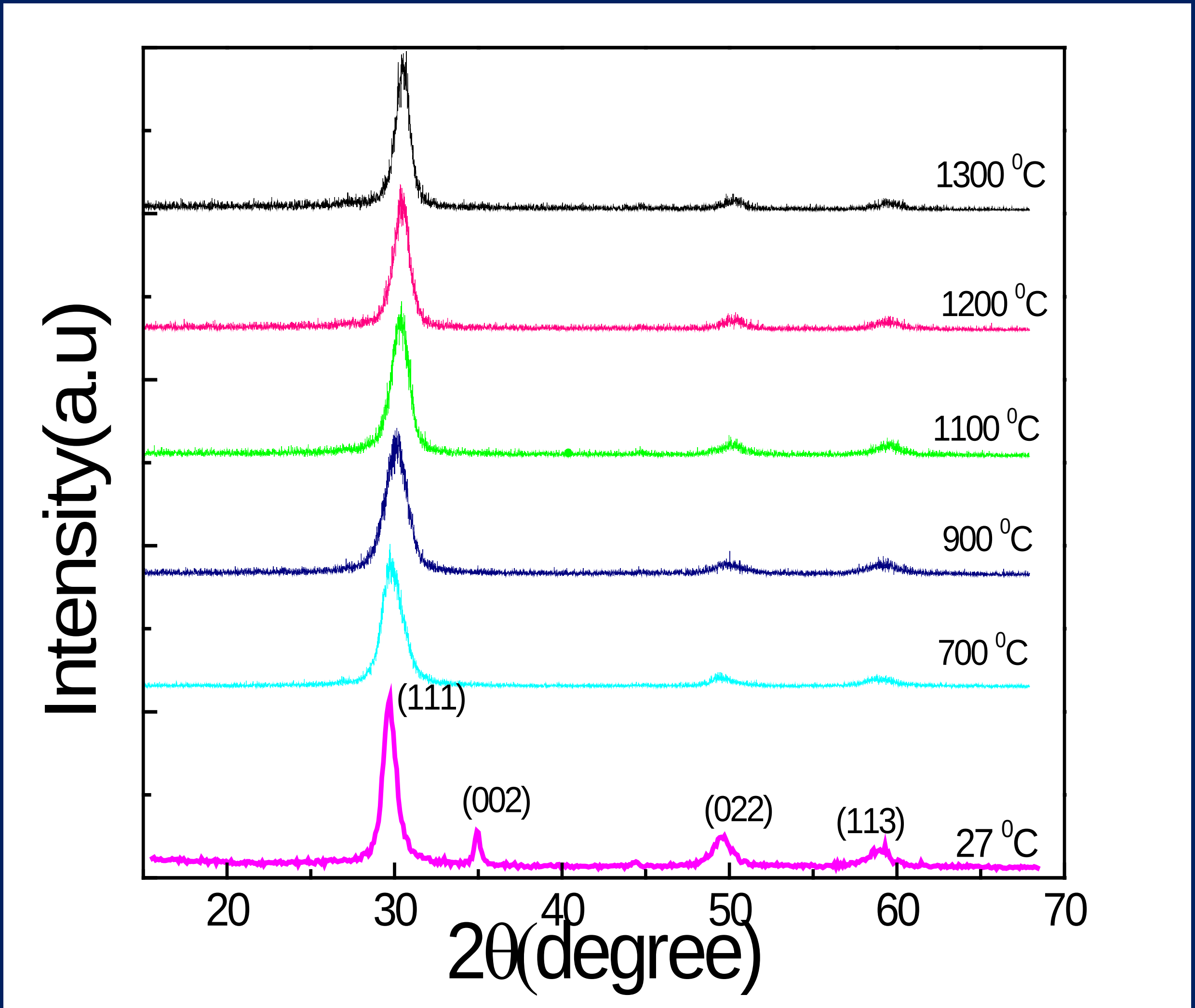


YHS + BC Inconel-738



Structural and Phase Stability

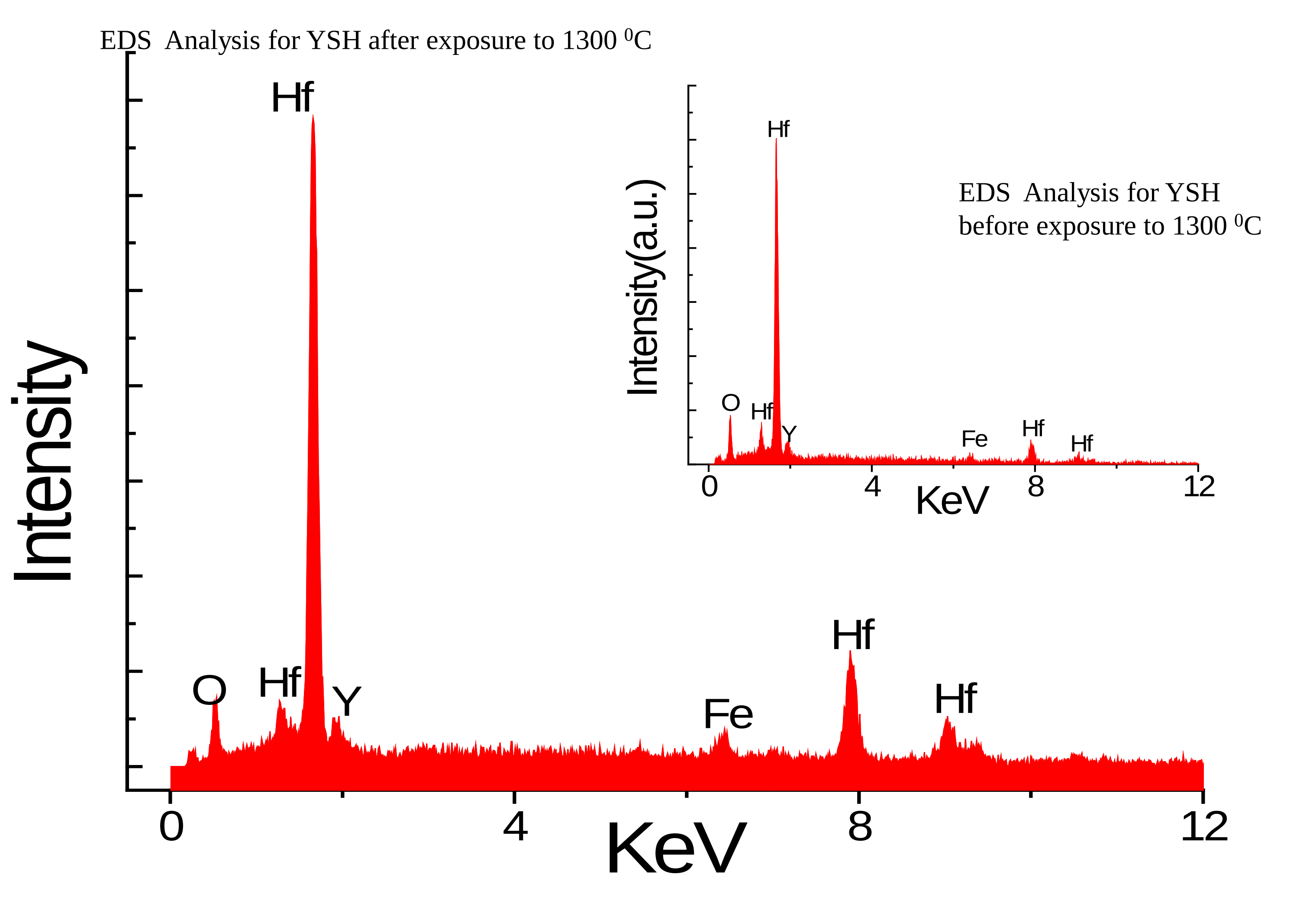
High temperature XRD for YSH



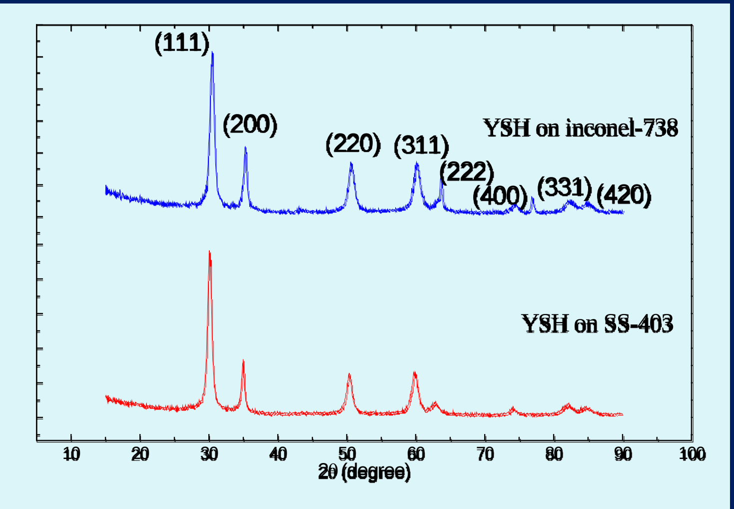
No change

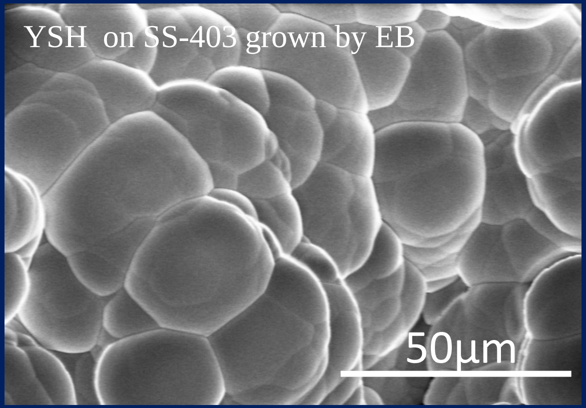
*Phase and chemical stability to 1300 ^{o}C

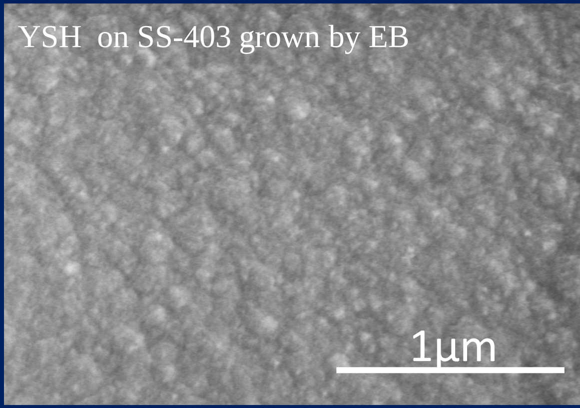
Chemical Stability

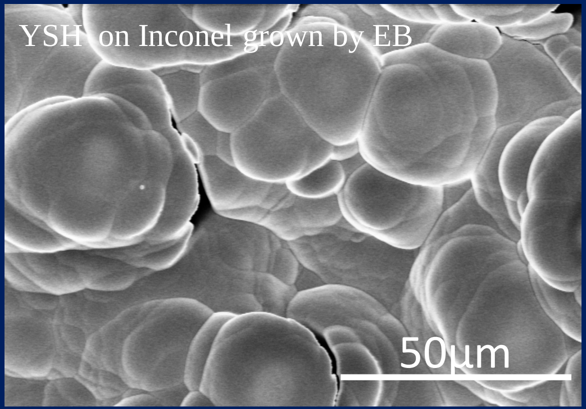


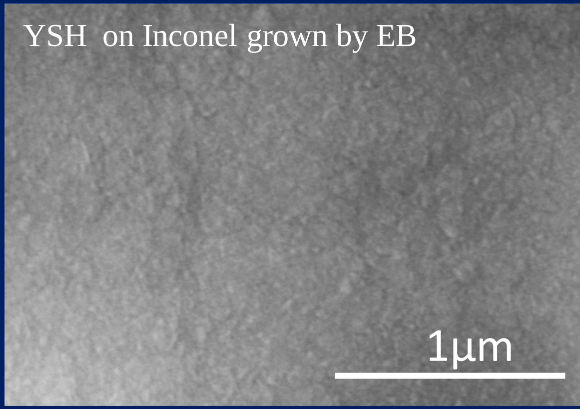
EBPVD Samples





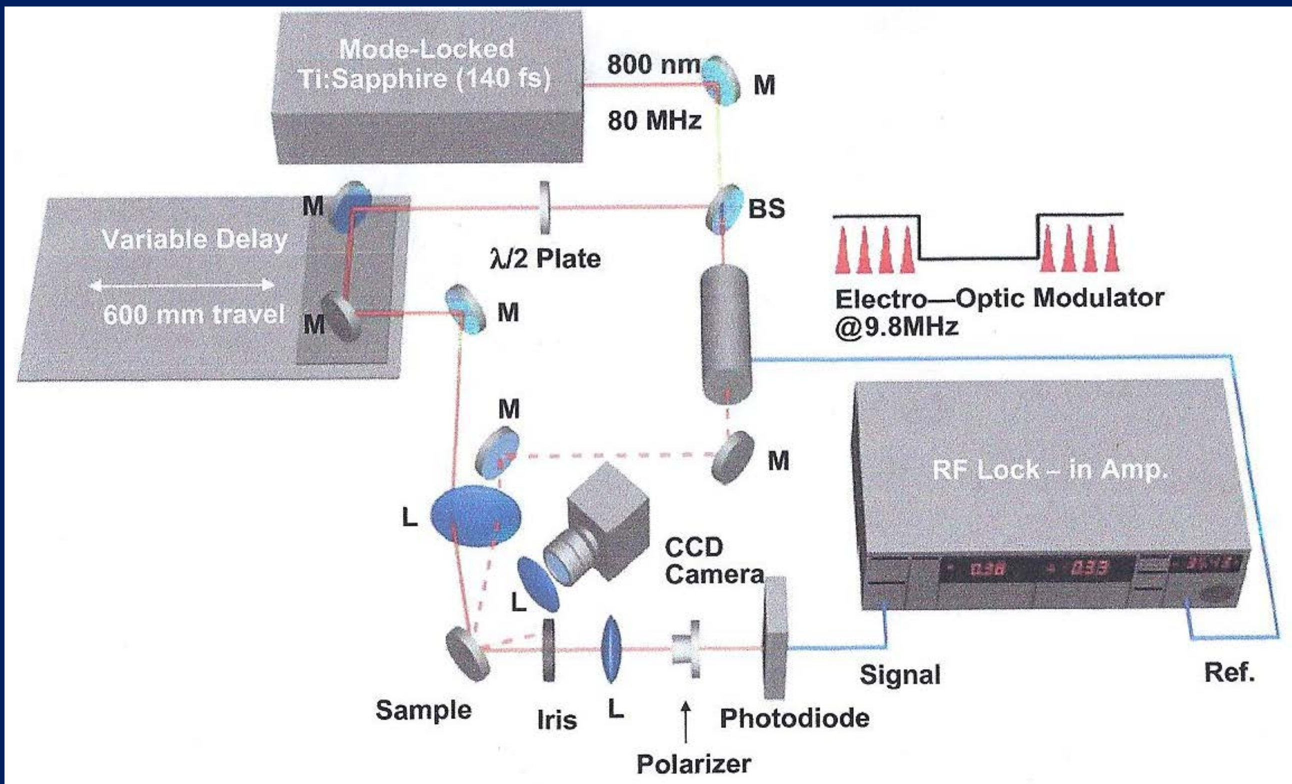






Thermal Conductivity - TDTR

Time-Domain Thermo-Reflectance



O/P (pumped by Nd:YVO_4 laser)

Pump → EOM

Probe → Var. De.

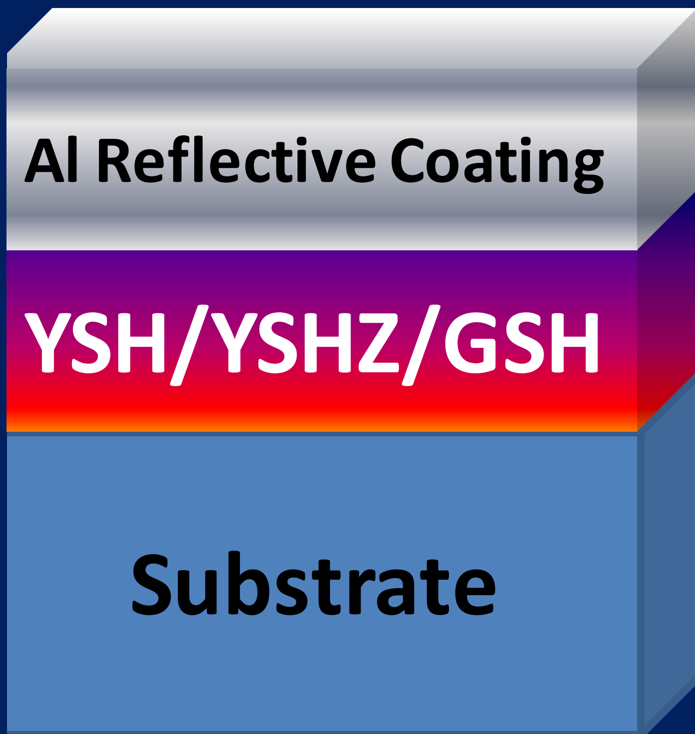
Time Difference

Pol. Ortho.

~50 µm
100 W

~20 µm
20 W

Thermal Conductivity – Sample Preparation & Data Analysis



<u>Frequency-domain model</u>

Ratio of the in-phase and out-of-phase lock-in amplifier signals is calculated as a function of time:

$$-\frac{V_{in}}{V_{out}} = \frac{\sum_{-m}^{m}\left(\Delta T(m/\tau + f) + \Delta T(m/\tau - f)\right)\exp(i2\pi mt/\tau)}{i\sum_{-m}^{m}\left(\Delta T(m/\tau + f) - \Delta T(m/\tau - f)\right)\exp(i2\pi mt/\tau)}$$

m: an integer denoting summation over pump pulses,

τ: time between unmodulated laser pulses (12.5 ns),

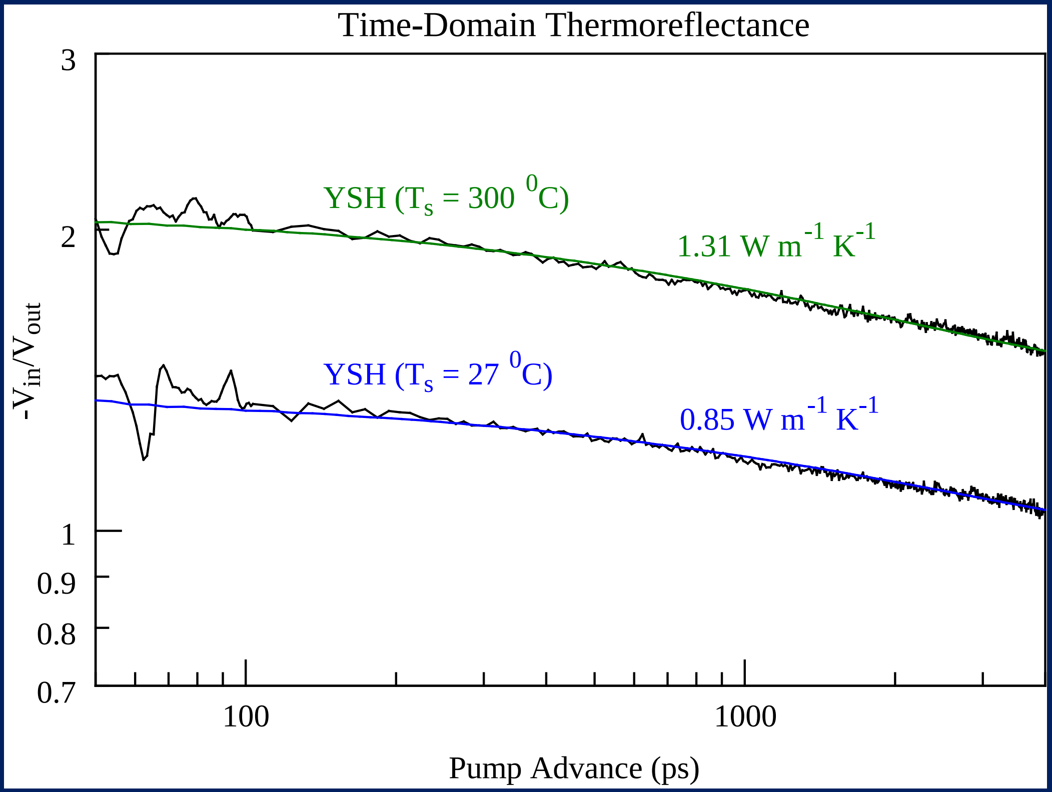
f: modulation frequency (9.8 MHz)

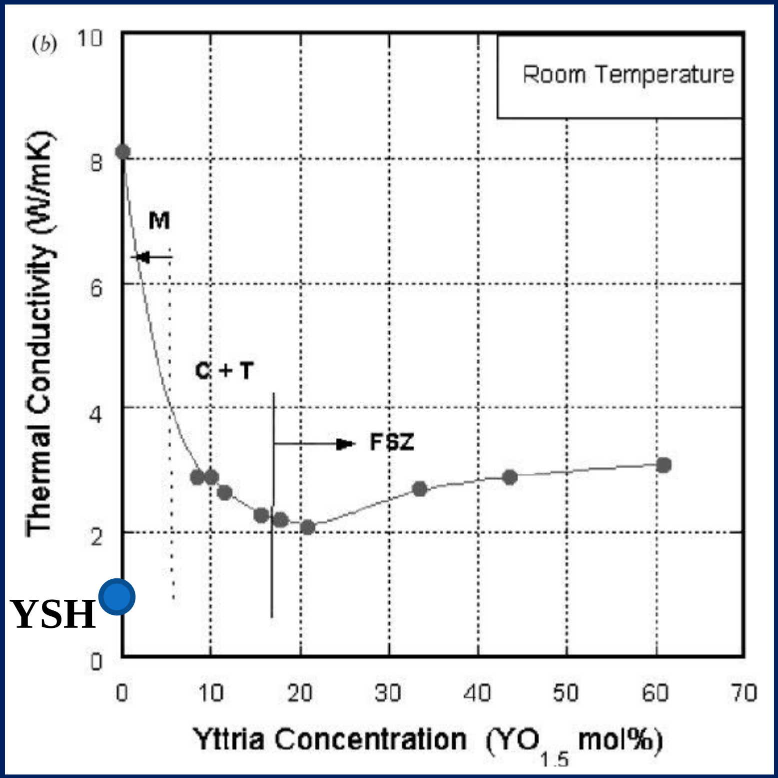
t: time delay (pump and probe pulses)

ΔT:

delay times <t=100 ps were not considered

Thermal Conductivity Data of YSH Coatings





C.V. Ramana et al., *ACS Appl. Mater. & Inter.* 4 (2011) 200-204

Thermal Conductivity – Photo-Acoustic Technique

$$\delta P = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{2\pi l_g T_0 k_s f \sin h\,(l_s \sigma_s)} \exp\left[j\left(\omega t - \frac{\pi}{2}\right)\right]$$

γ is the air specific heat ratio
P_o, the ambient pressure
T_o, the ambient temperature
I_o, the absorbed light intensity
$\omega = 2\pi f$, where f is the modulation frequency
l_i, k_i and α_i are the length, thermal conductivity and the thermal diffusivity of the sample respectively.
subscript i (=s, g) denotes sample (s) and gas (s) medium
$\sigma_i = (1 + j)a_i$ is the complex thermal diffusion coefficient
$a_i = (\omega/2\alpha s)^{1/2}$

For thick sample,

$$\delta P \cong \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{\frac{1}{2}}}{\pi l_g T_0 k_s} \frac{\exp - l_s \left(\frac{\pi f}{\alpha_s}\right)^{\frac{1}{2}}}{f} \; x \exp[j \left(\omega t - \frac{\pi}{2} - l_s a_s\right)]$$

l_s, thickness of the sample

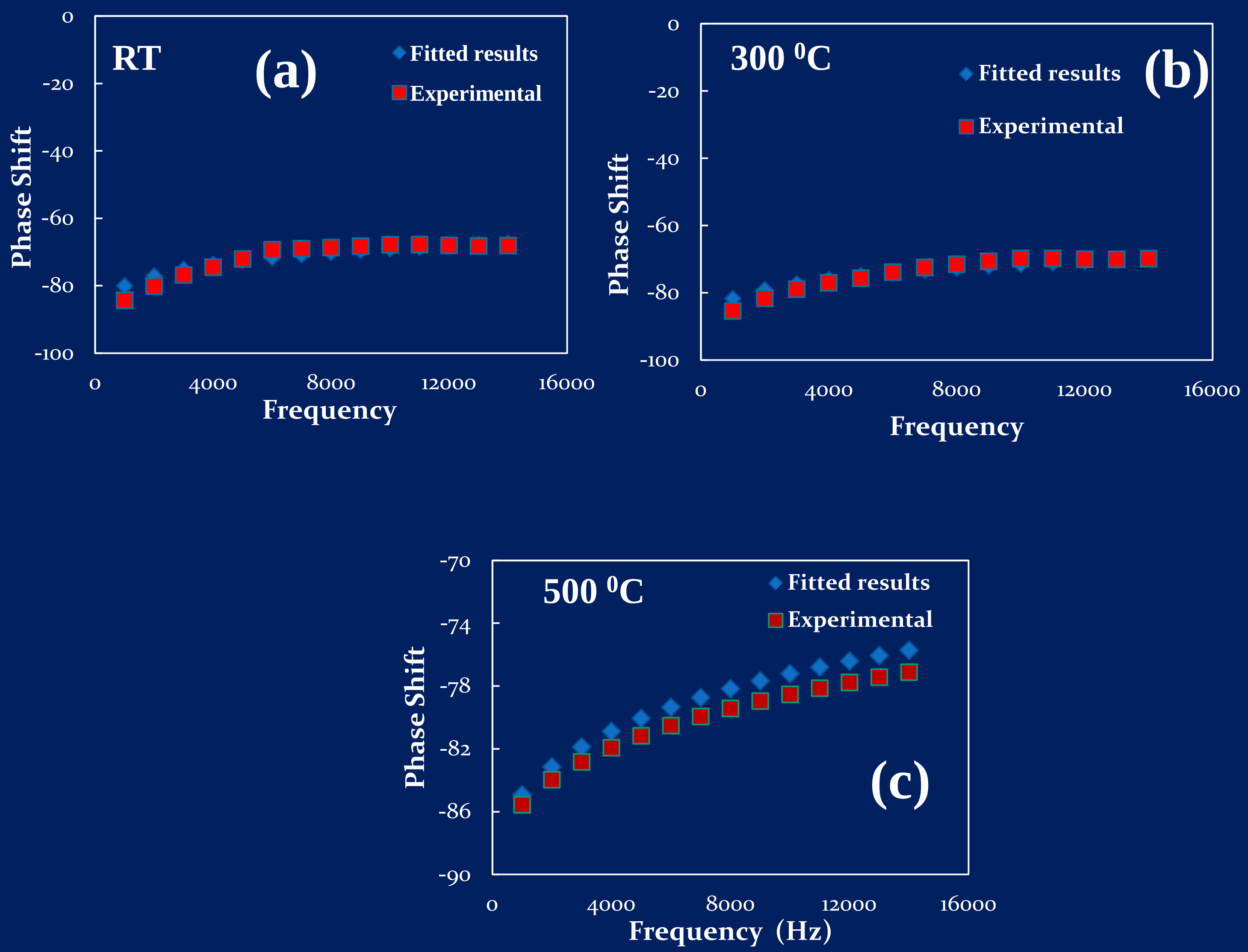
So, amplitude varies as:

$$\left(\frac{1}{f}\right) \exp[l_s (\frac{\pi f}{\alpha_s})^{1/2}]$$

Phase varies as:

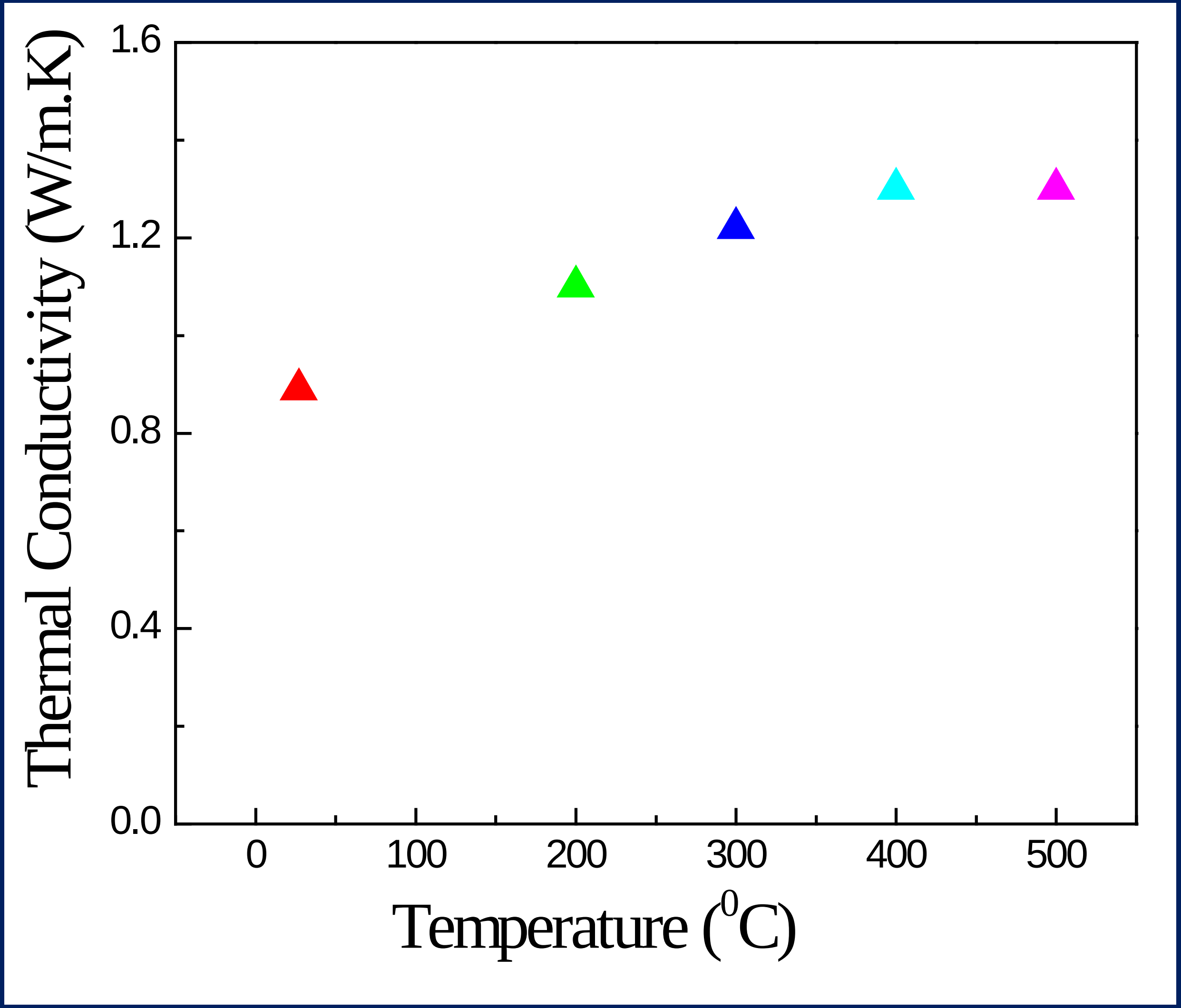
$$-l_s (\frac{\pi f}{\alpha_s})^{1/2}$$

YSH coatings on Inconel-738



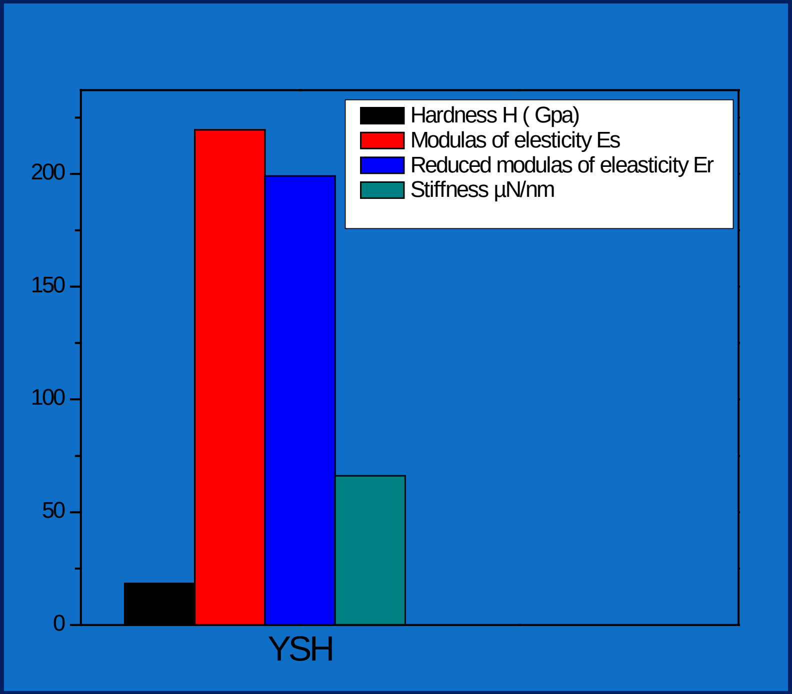
M. Noor-A-Alam et al., *Ceram. Inter.* 38 (2012) 2957–2961

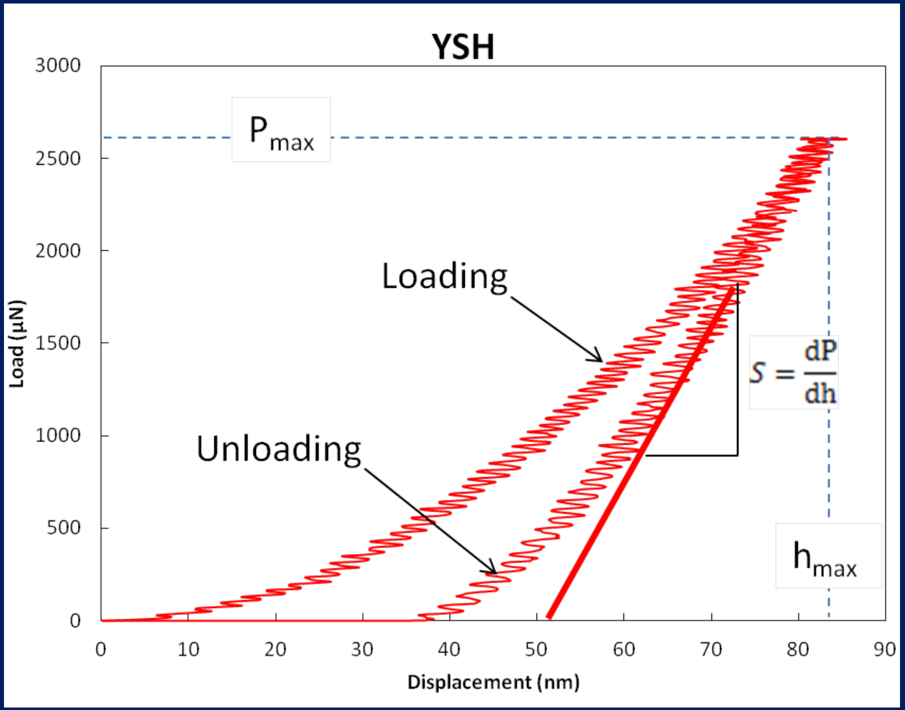
Thermal Conductivity – YSH



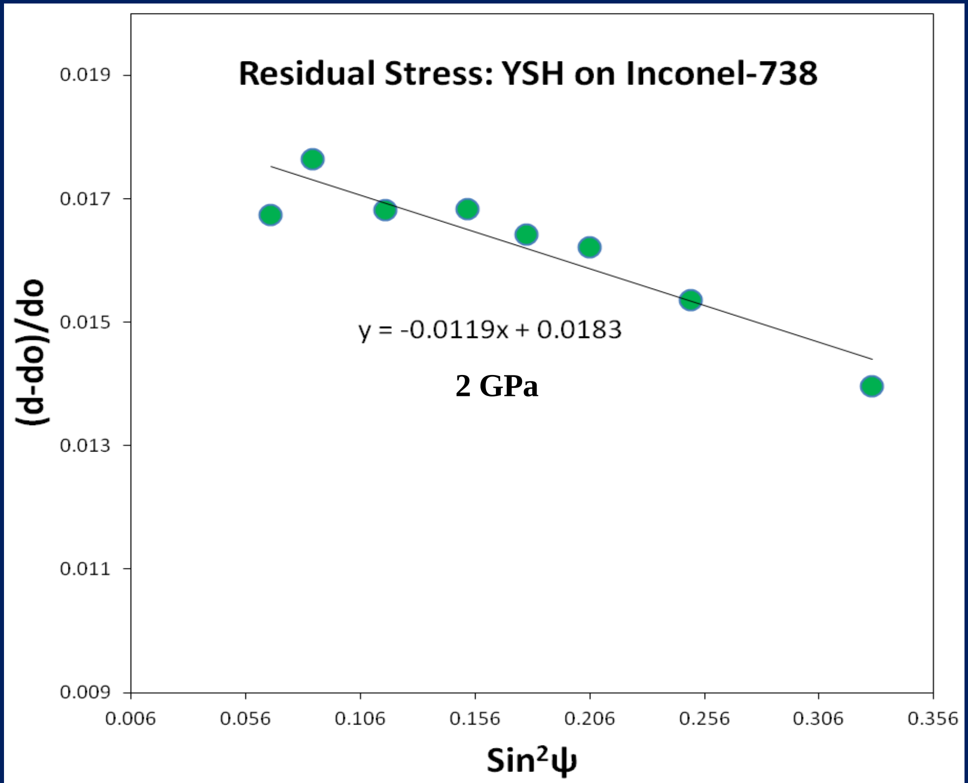
M. Noor-A-Alam et al., *Ceram. Inter.* 38 (2012) 2957–2961

Mechanical Properties – YSH Coatings





Residual Stress Analysis



$$\frac{d_{\phi\psi} - d_0}{d_0} = \frac{1+\nu}{E}\sigma_\phi \sin^2\psi - \frac{\nu}{E}(\sigma_{11} + \sigma_{22})$$

d_0 = Unstressed lattice spacing

$d_{\phi\psi}$ =Stressed lattice spacing

σ_ϕ = Stress component along the direction ϕ defined in the plane of coating

Ψ = Tilt angle

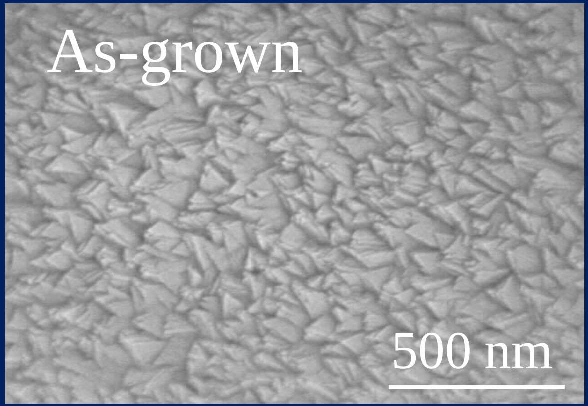
E = Young's modulus

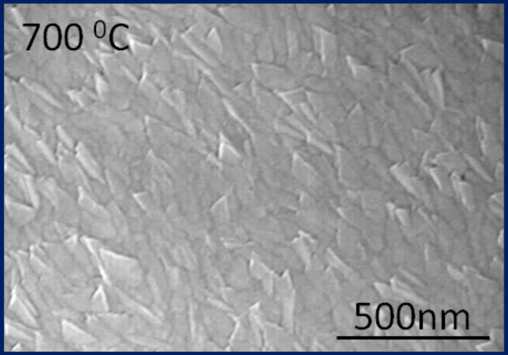
ν = Poisson ratio

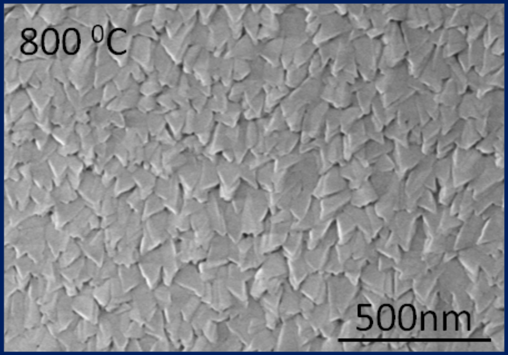
σ_{11} and σ_{22} are in-plane principal stress components

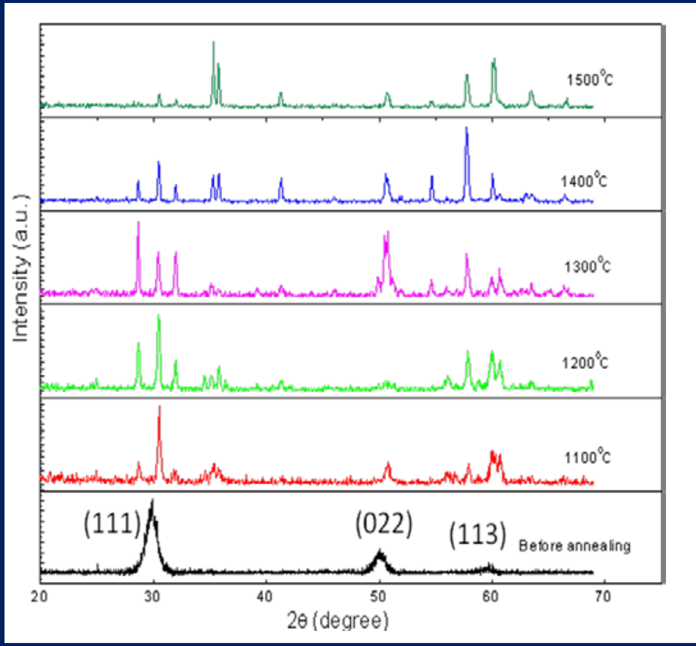
Furnace Heating - YSH

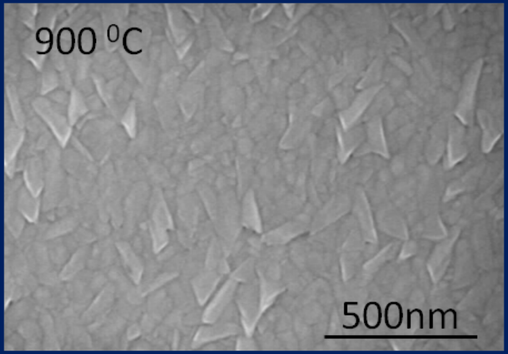
12 hours

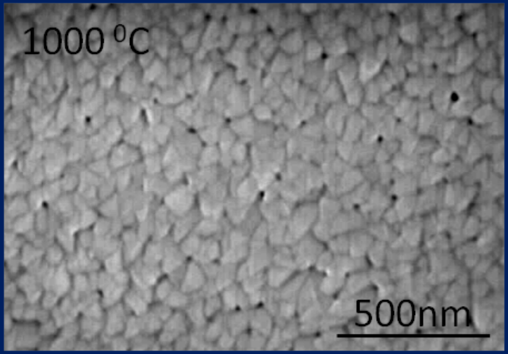


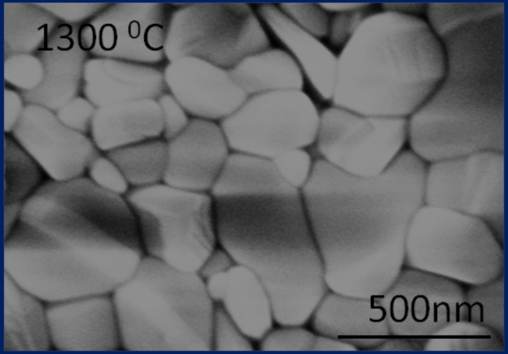


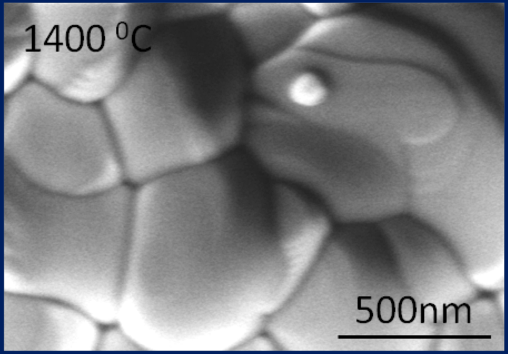






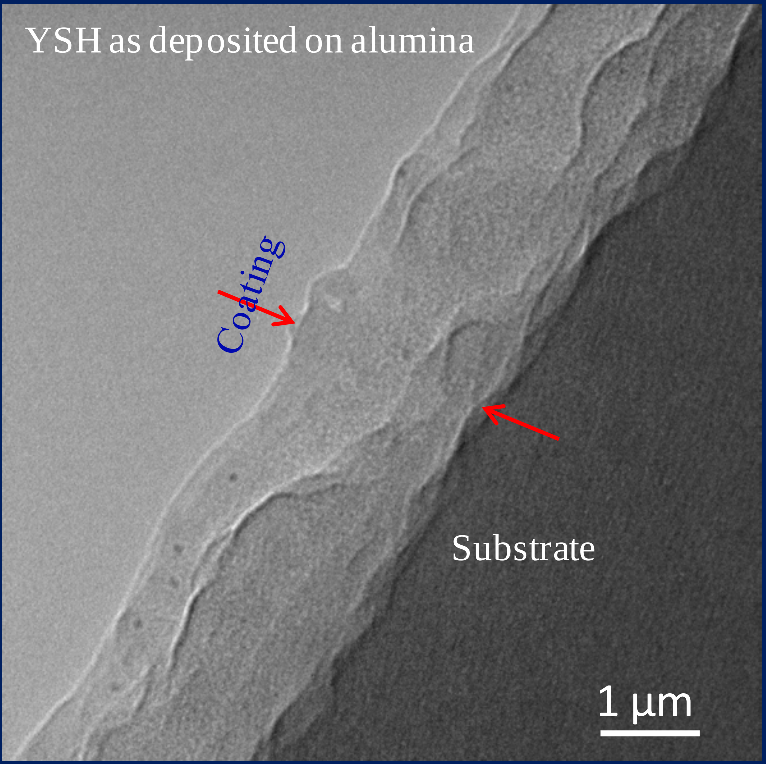


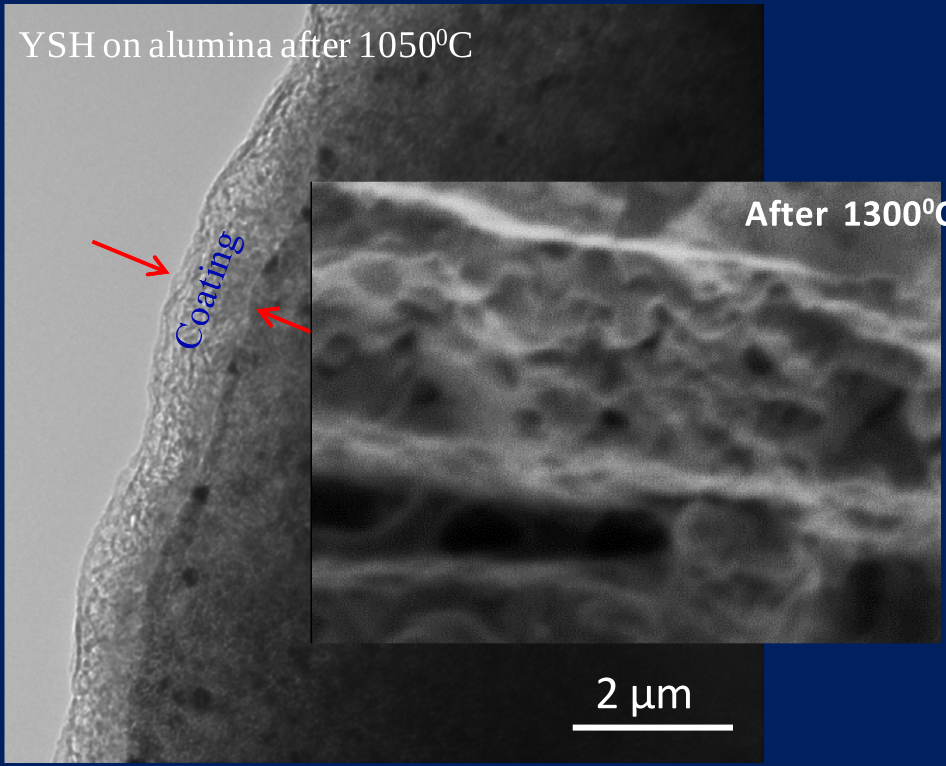




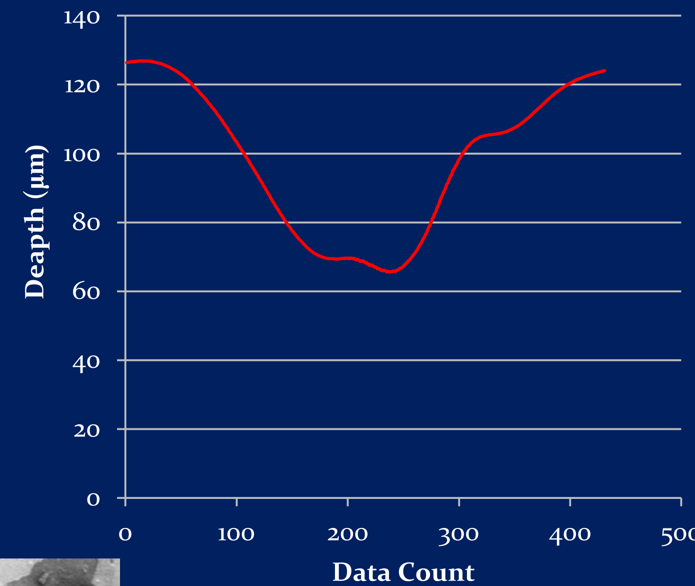
TEM Analysis: TGO-TBC Interface

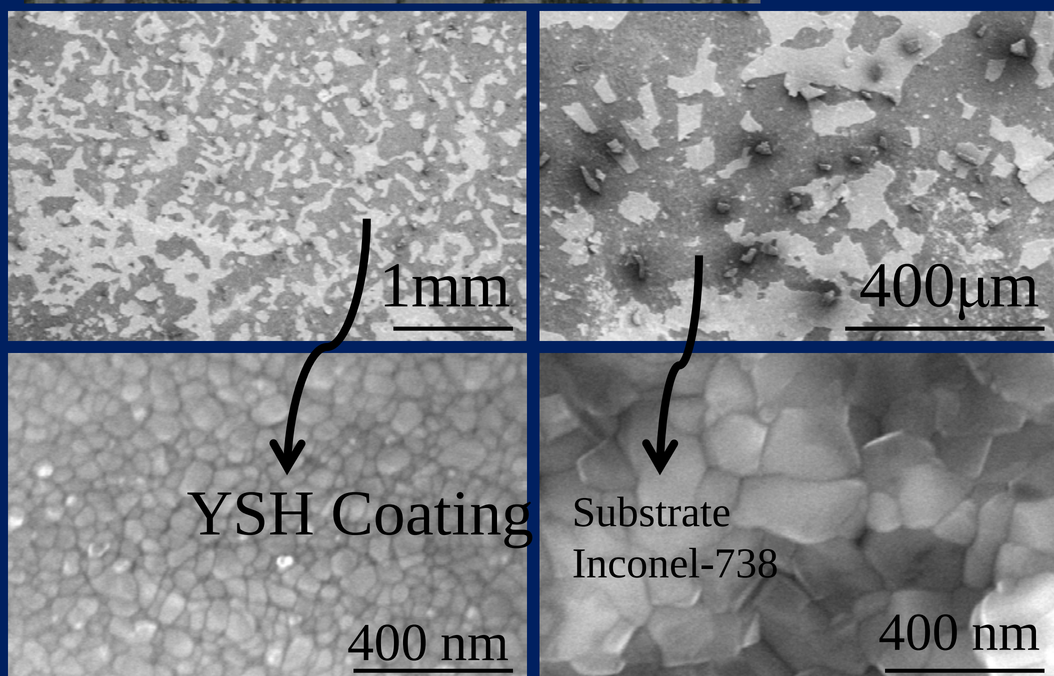
* Bond coat enhances the TBC adhesion and oxidation resistance.
* Stresses due to CTE difference cause delamination or buckling at the TGO-TBC interface





High Temperature Impact Measurements



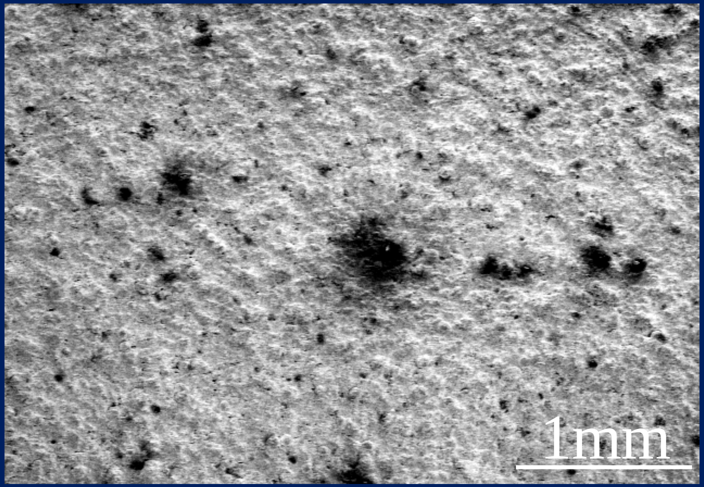


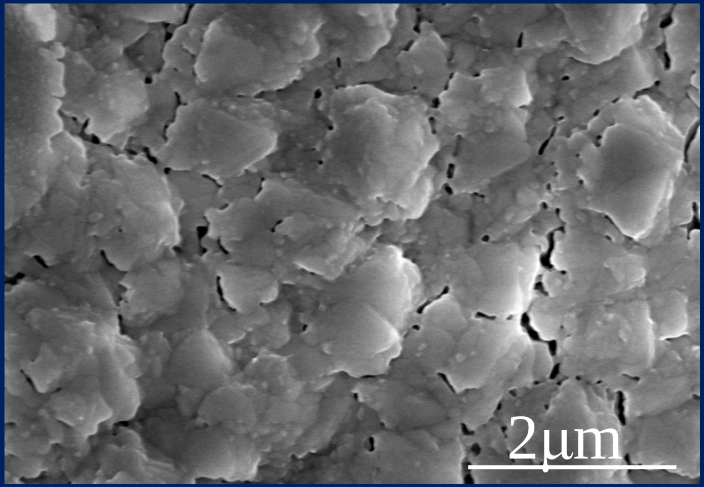
YSH//Inconel-738 after impact test at 800 ^{0}C at a velocity of 115 m/s

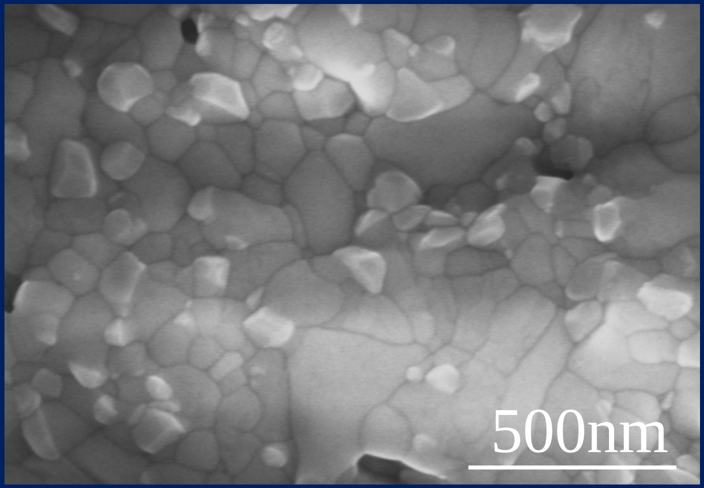
Projectile (SS): (1/16) in. dia.

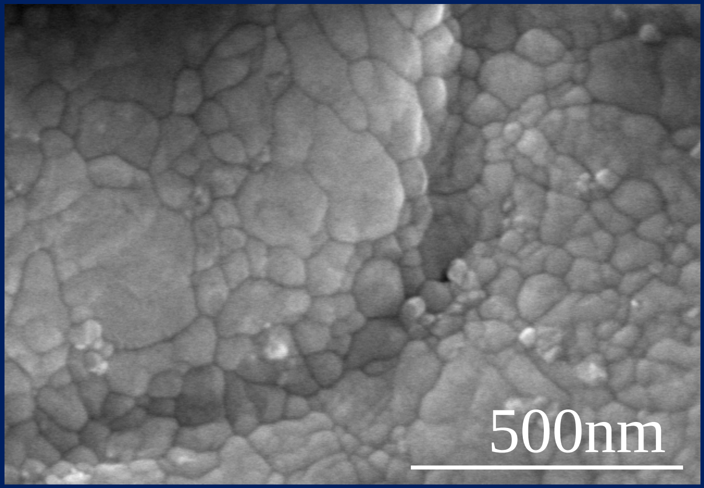
$$\sigma_p = (E\alpha\Delta T)/(1-\upsilon)$$

High Temperature Impact Measurements YSH TBC//BC//IN-738

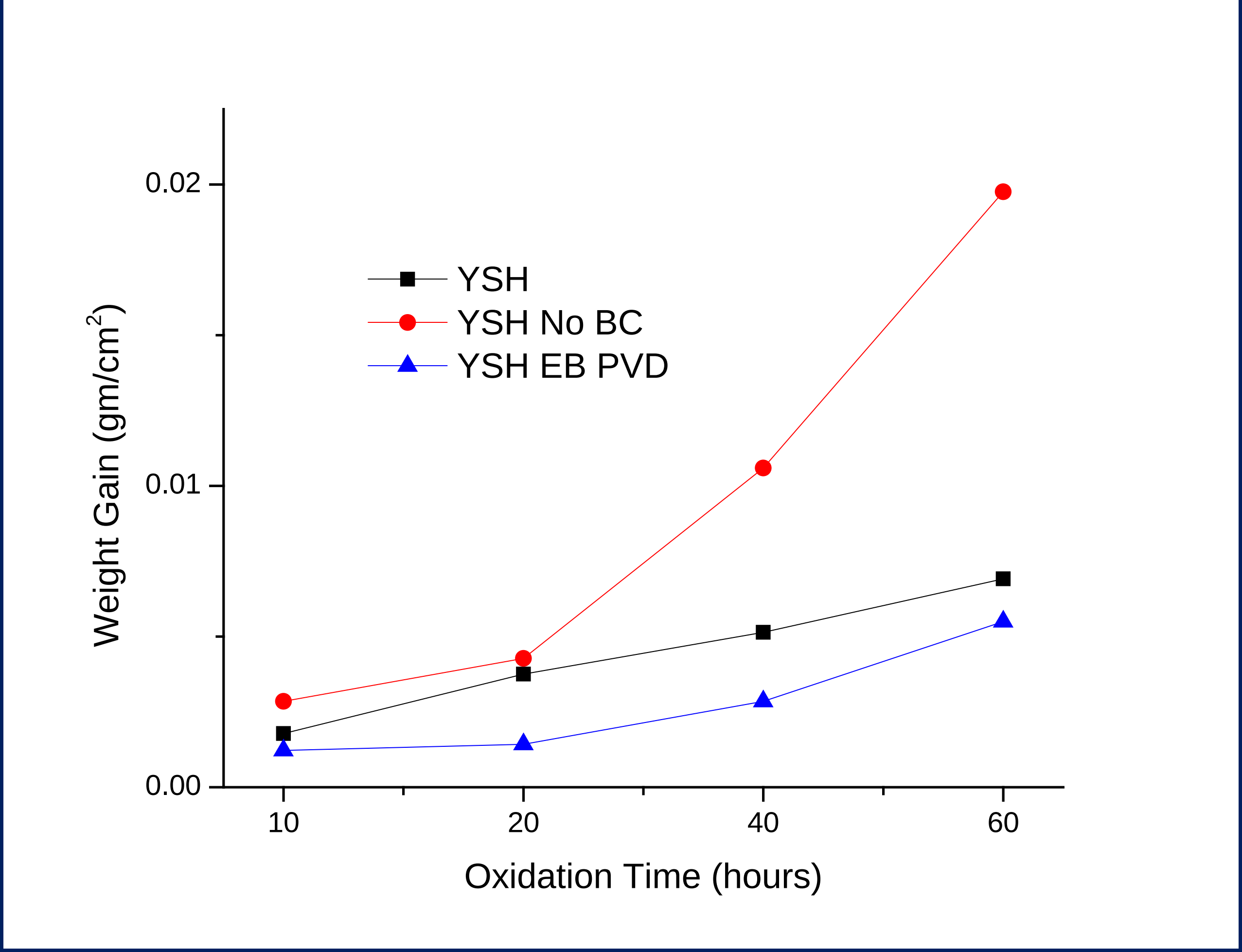






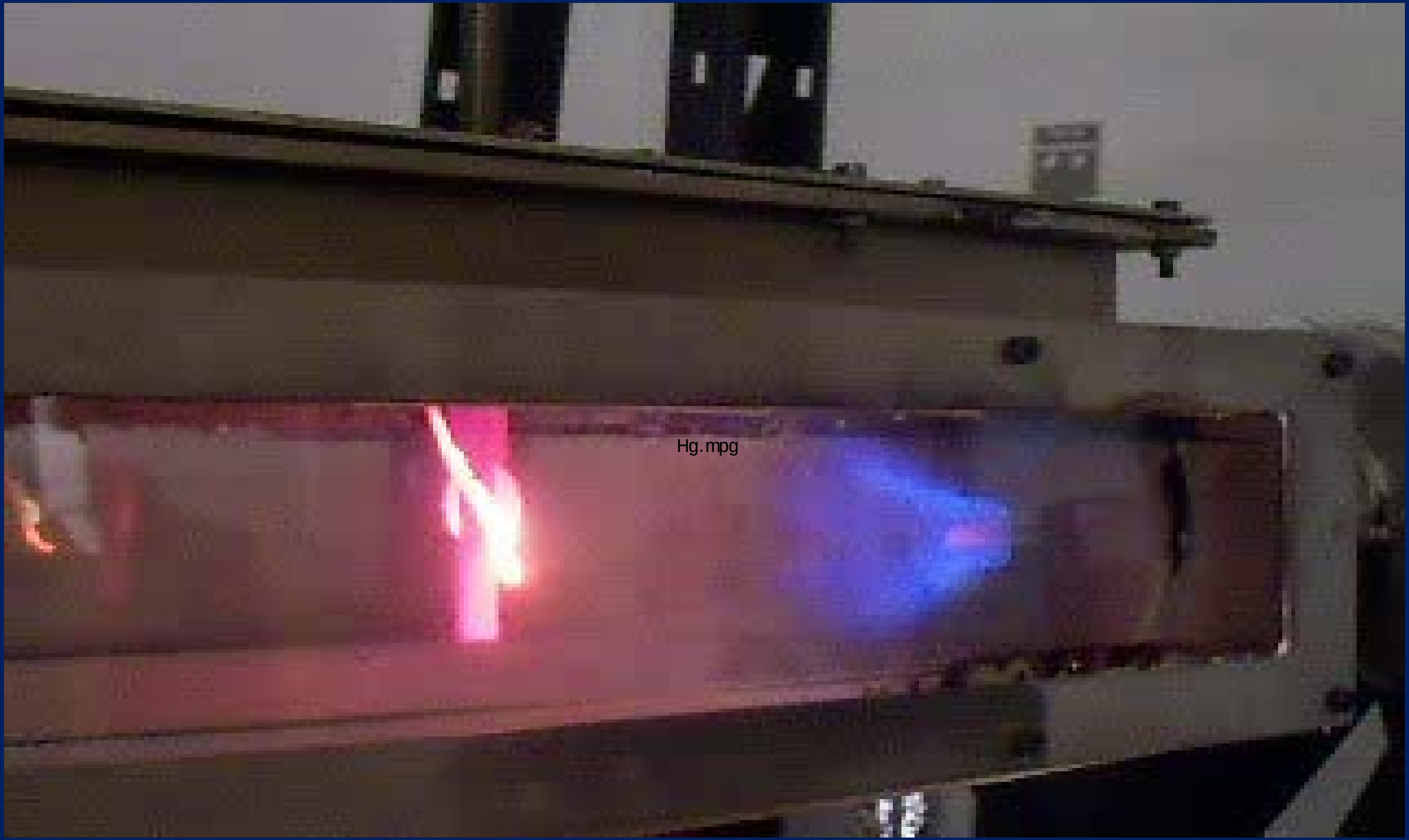


Oxidation

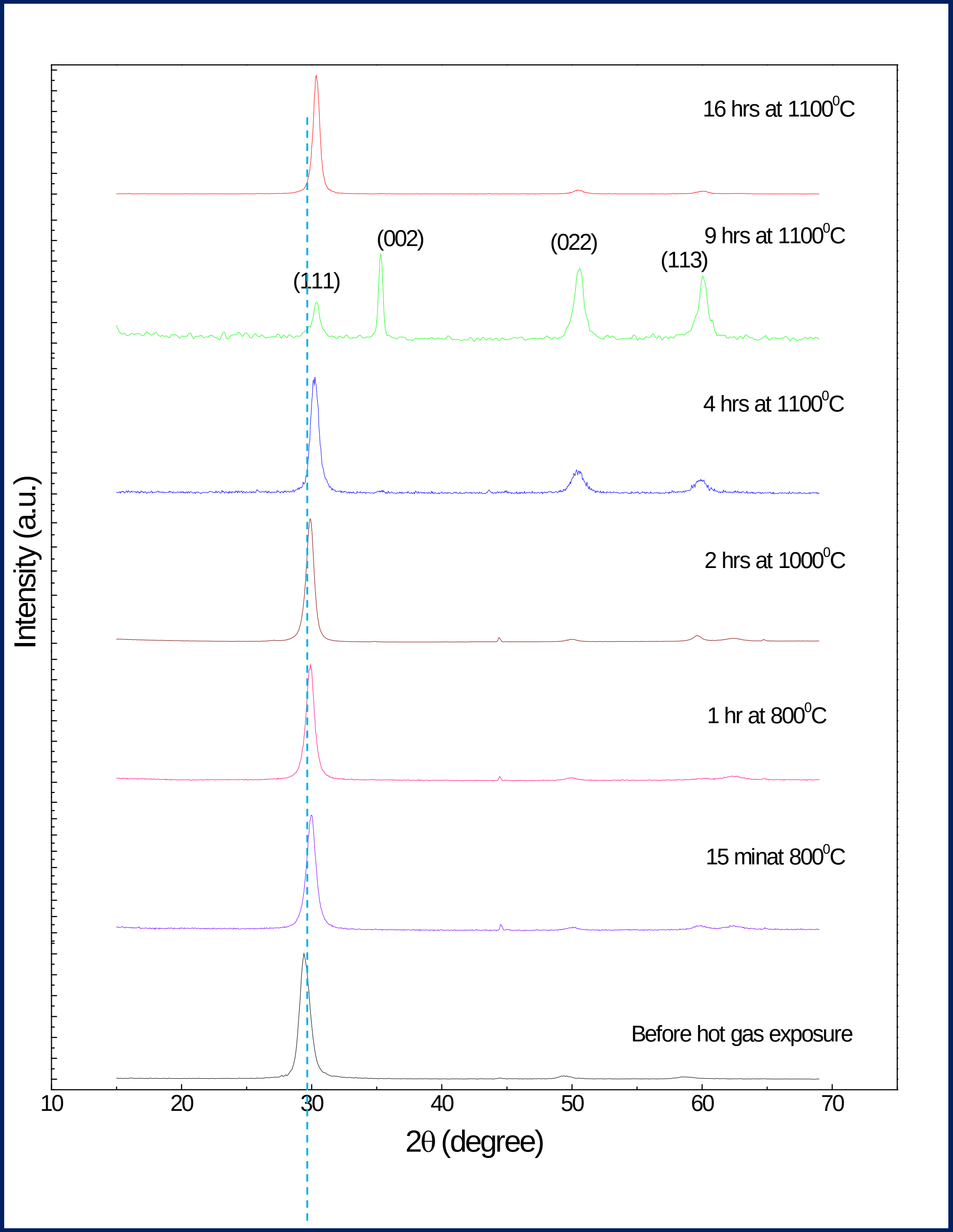


YSH
YSH No BC
YSH EB PVD
Weight Gain (gm/cm^2)
0.02
0.01
0.00
10
20
40
60
Oxidation Time (hours)

Hot Gas Exposure



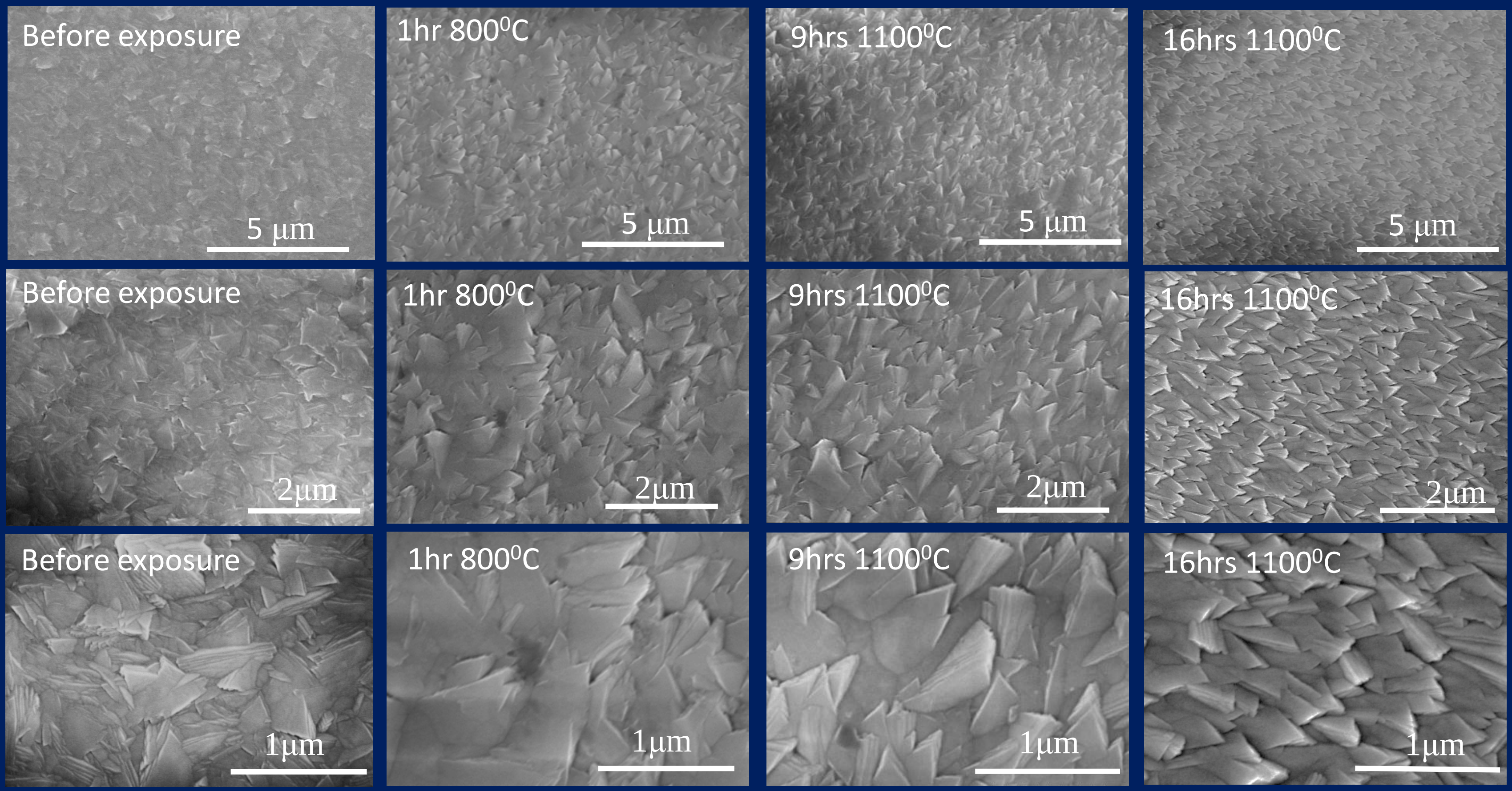
XRD



16 hrs at 1100°C
9 hrs at 1100°C
(002)
(022)
(113)
(111)
4 hrs at 1100°C
2 hrs at 1000°C
1 hr at 800°C
15 minat 800°C
Before hot gas exposure
Intensity (a.u.)
10
20
30
40
50
60
70
2θ (degree)

Morphology (Under Hot Gas Exposure)

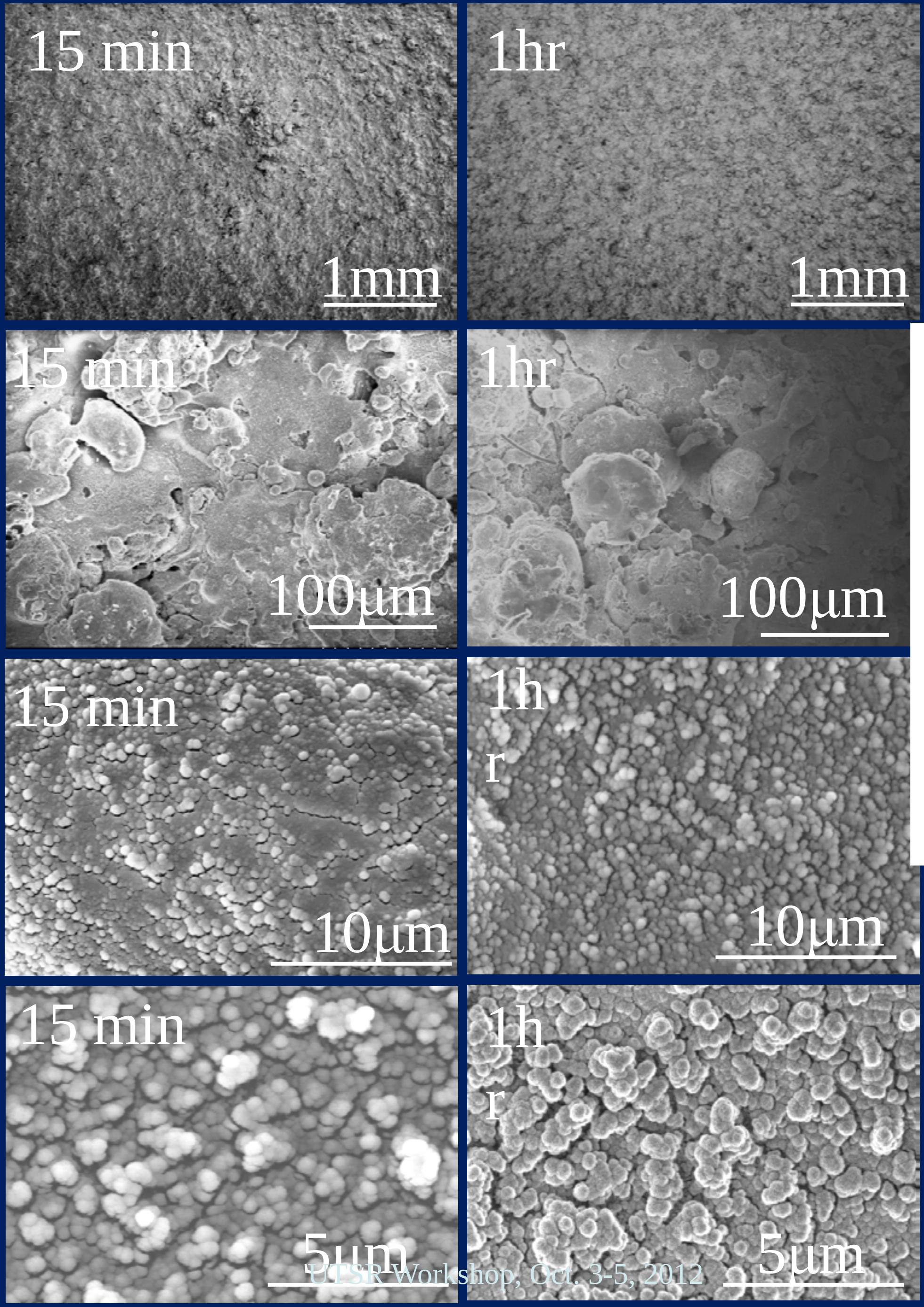
Set - 1

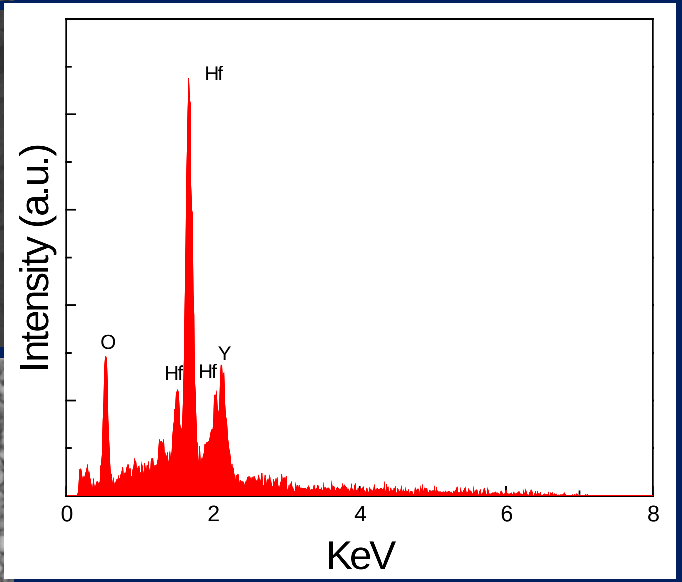


(a) (b) (c) (d)

Hot Gas Exposure

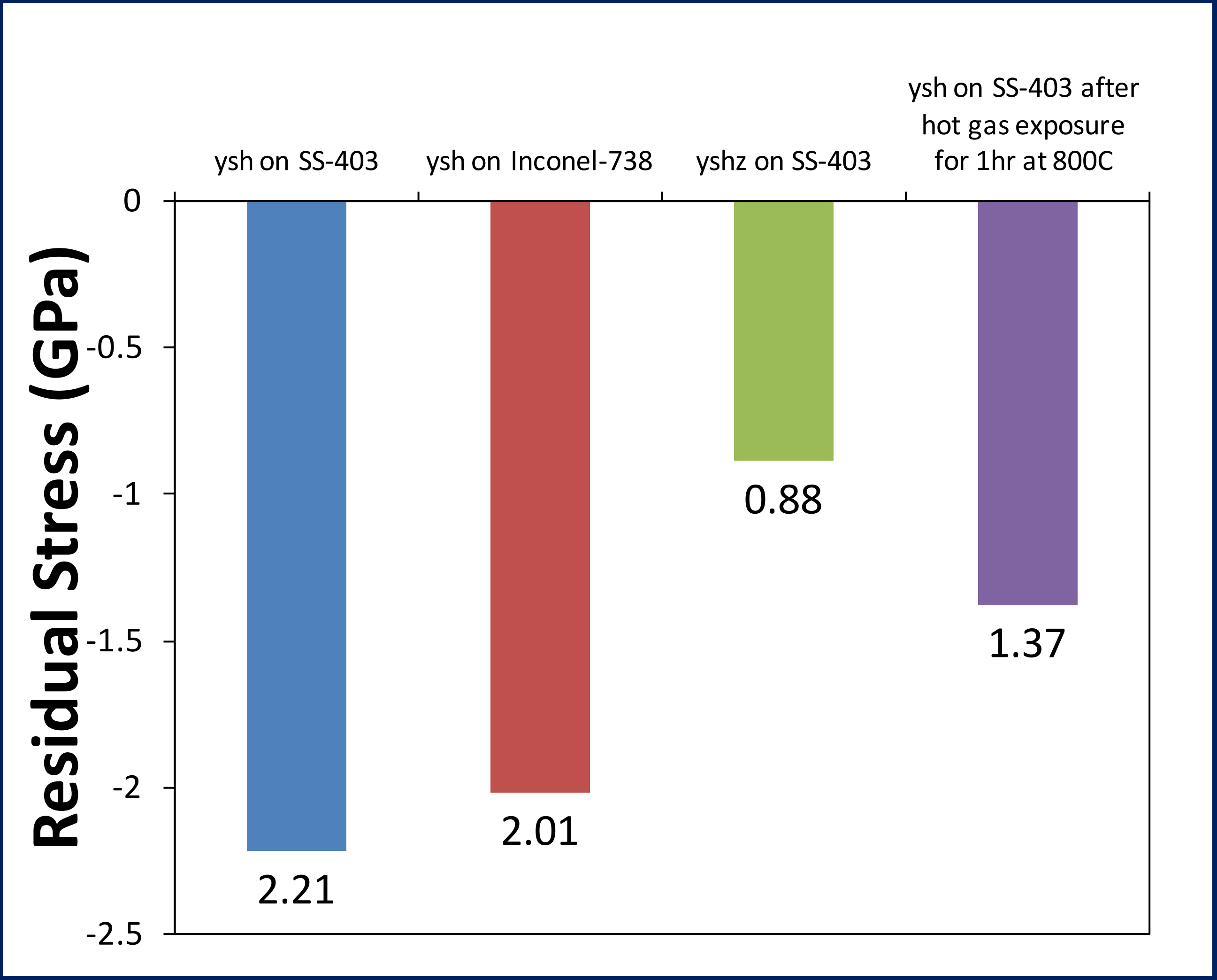
Set-2



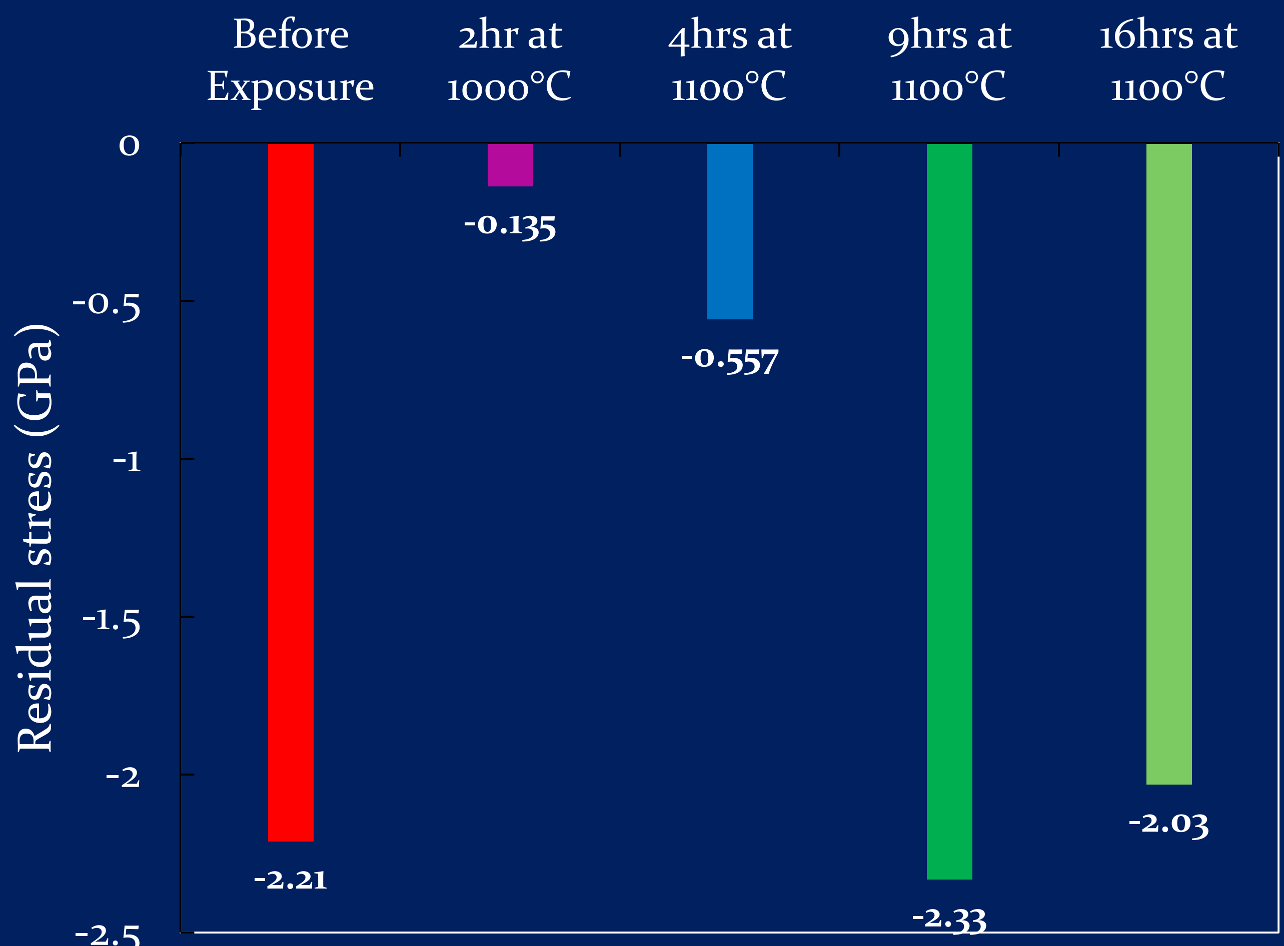


Carbon deposited onto the surface!

Stress Evolution – Comparison

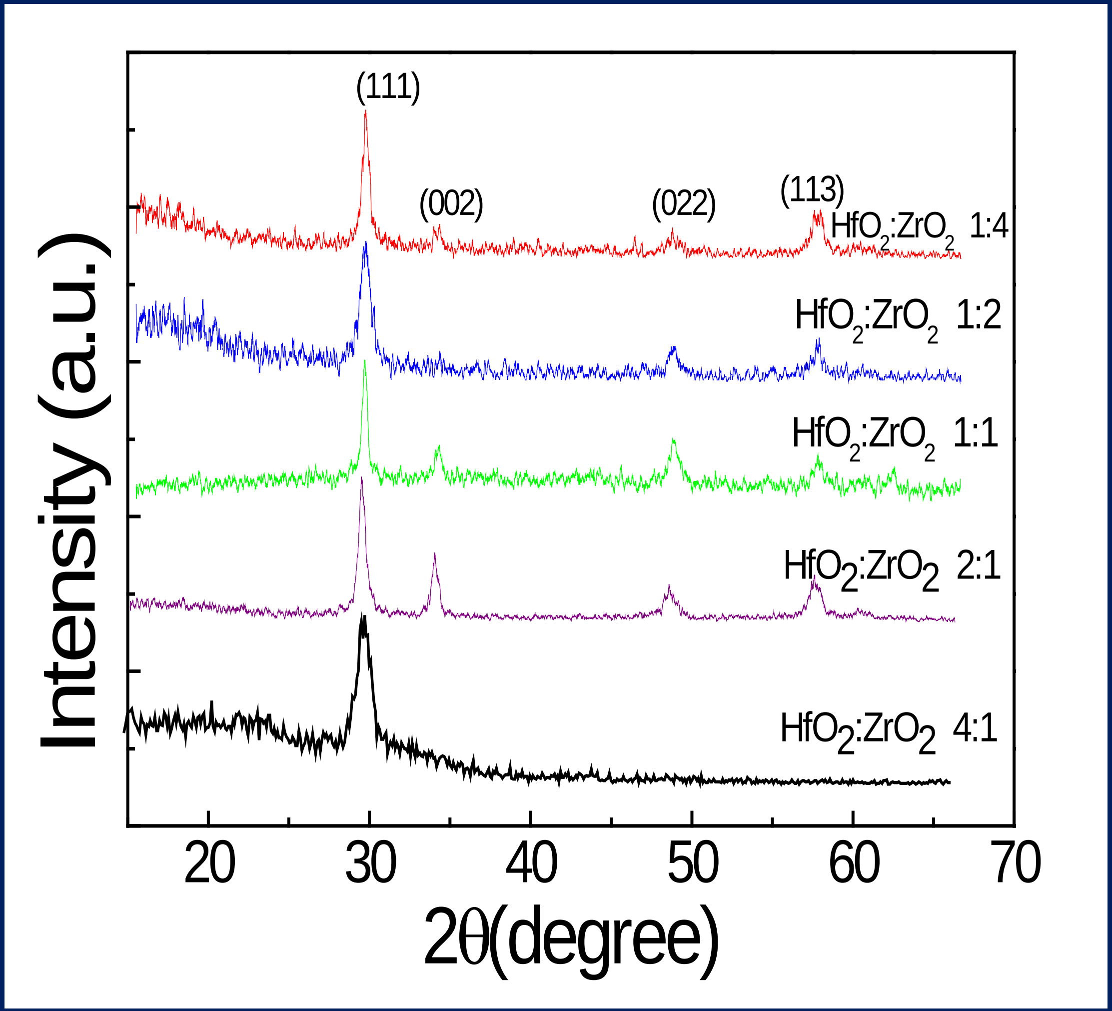


Stress Evolution – Comparison



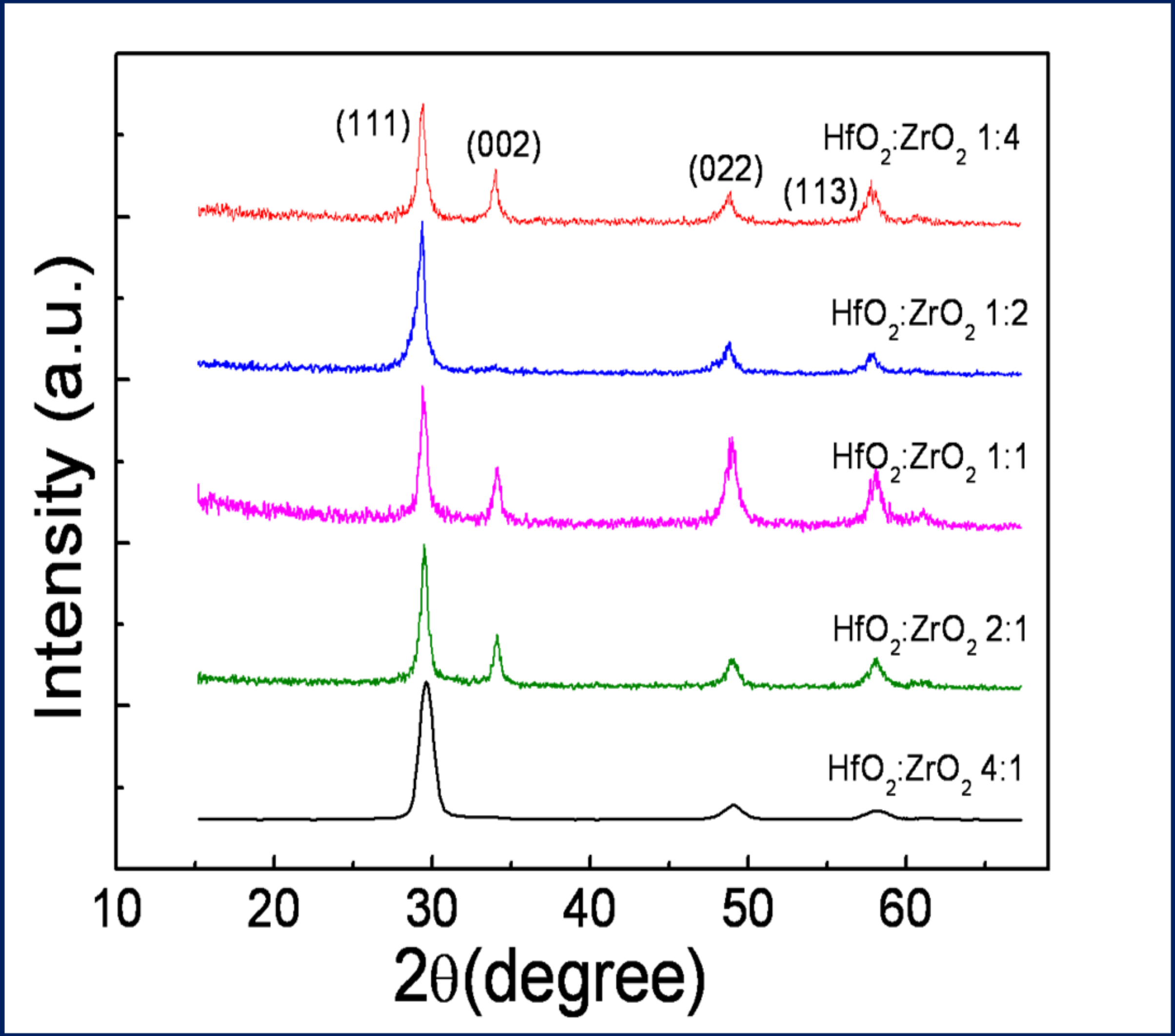
YSHZ

Structure and Phase Analysis



M. Noor-A-Alam et al., *Surf. Coat. Technol.* 206 (2011) 1628–1633

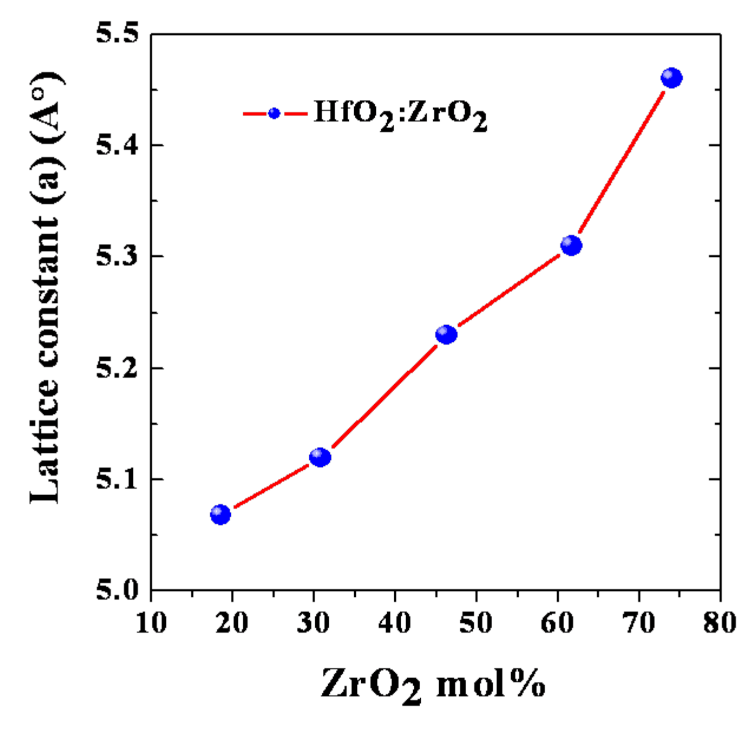
YSHZ on Alumina Substrates

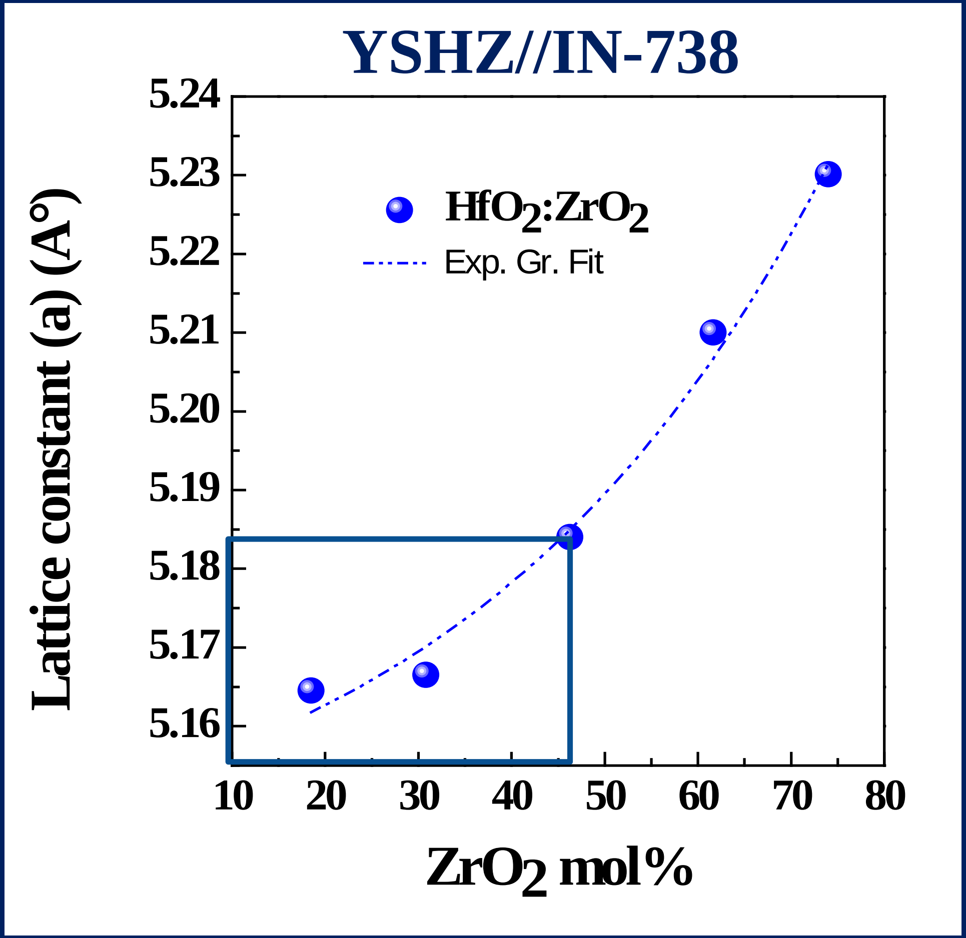


M. Noor-A-Alam et al., *Surf. Coat. Technol.* 206 (2011) 1628–1633

Effect of Composition

Lattice Expansion
Strain
Exponential

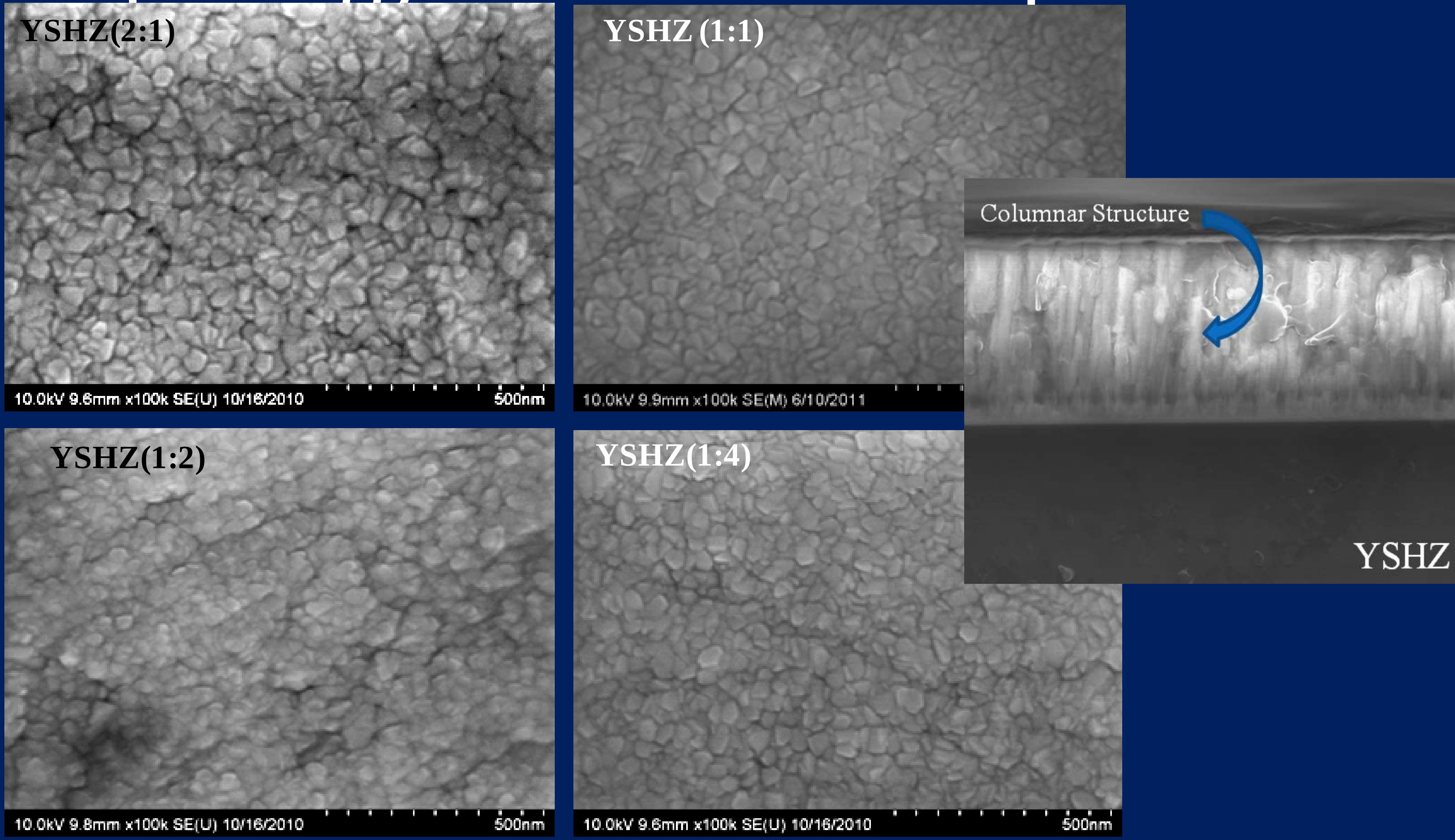




M. Noor-A-Alam et al., *Surf. Coat. Technol.* 206 (2011) 1628–1633

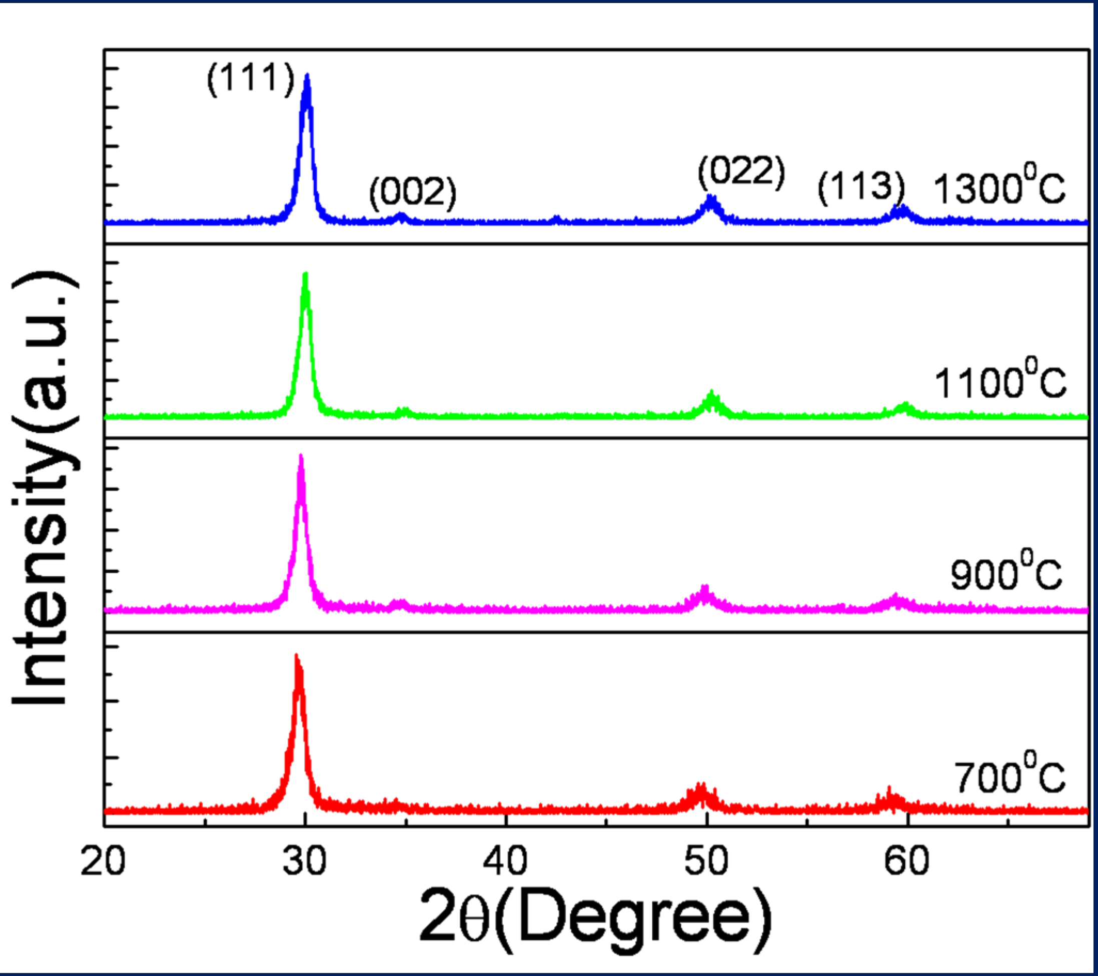
Size difference of Y, Hf and Zr ions

Morphology – Effect of Composition



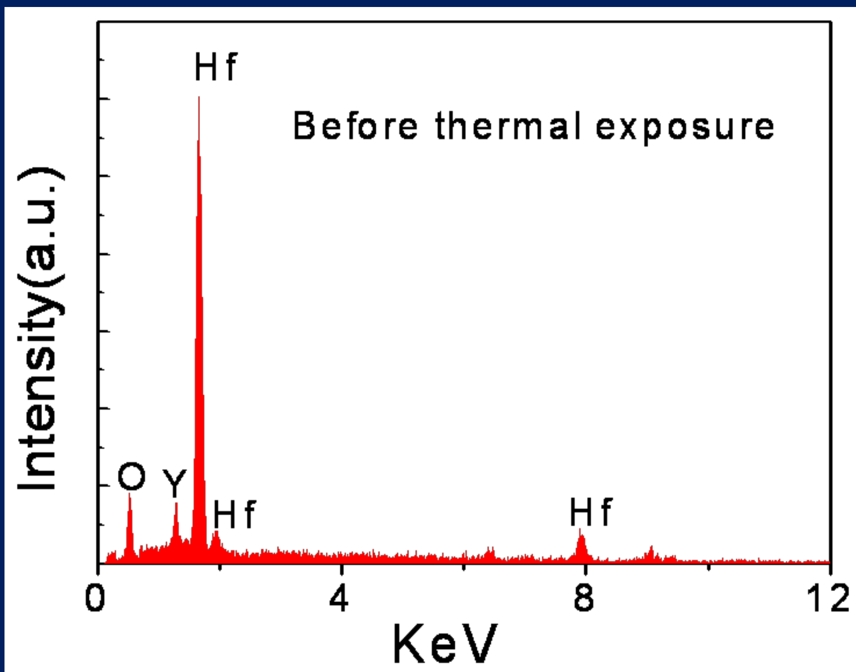
M. Noor-A-Alam et al., *Surf. Coat. Technol.* 206 (2011) 1628–1633

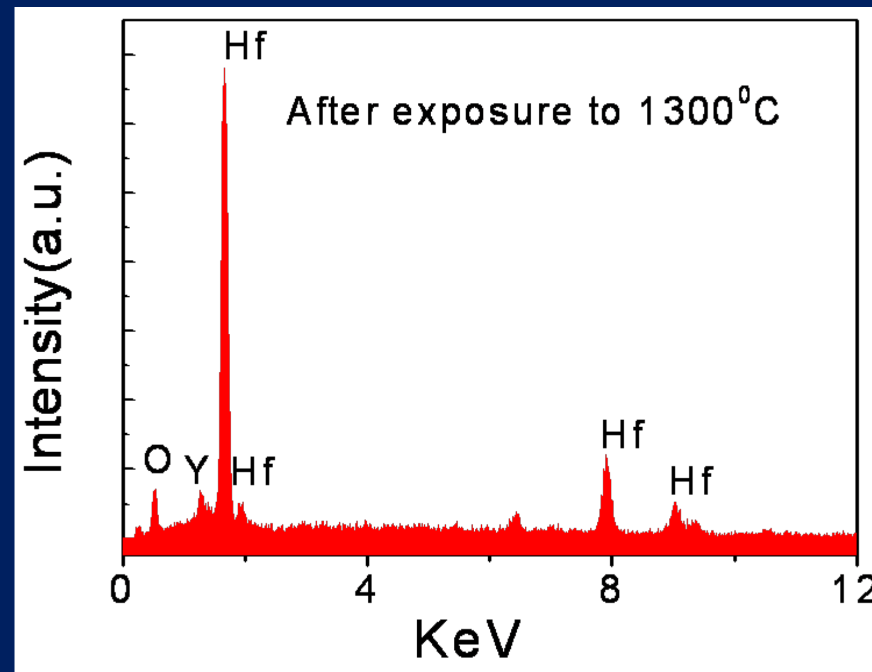
Thermal Phase Stability - YSHZ



M. Noor-A-Alam et al., *Surf. Coat. Technol.* 206 (2011) 1628–1633

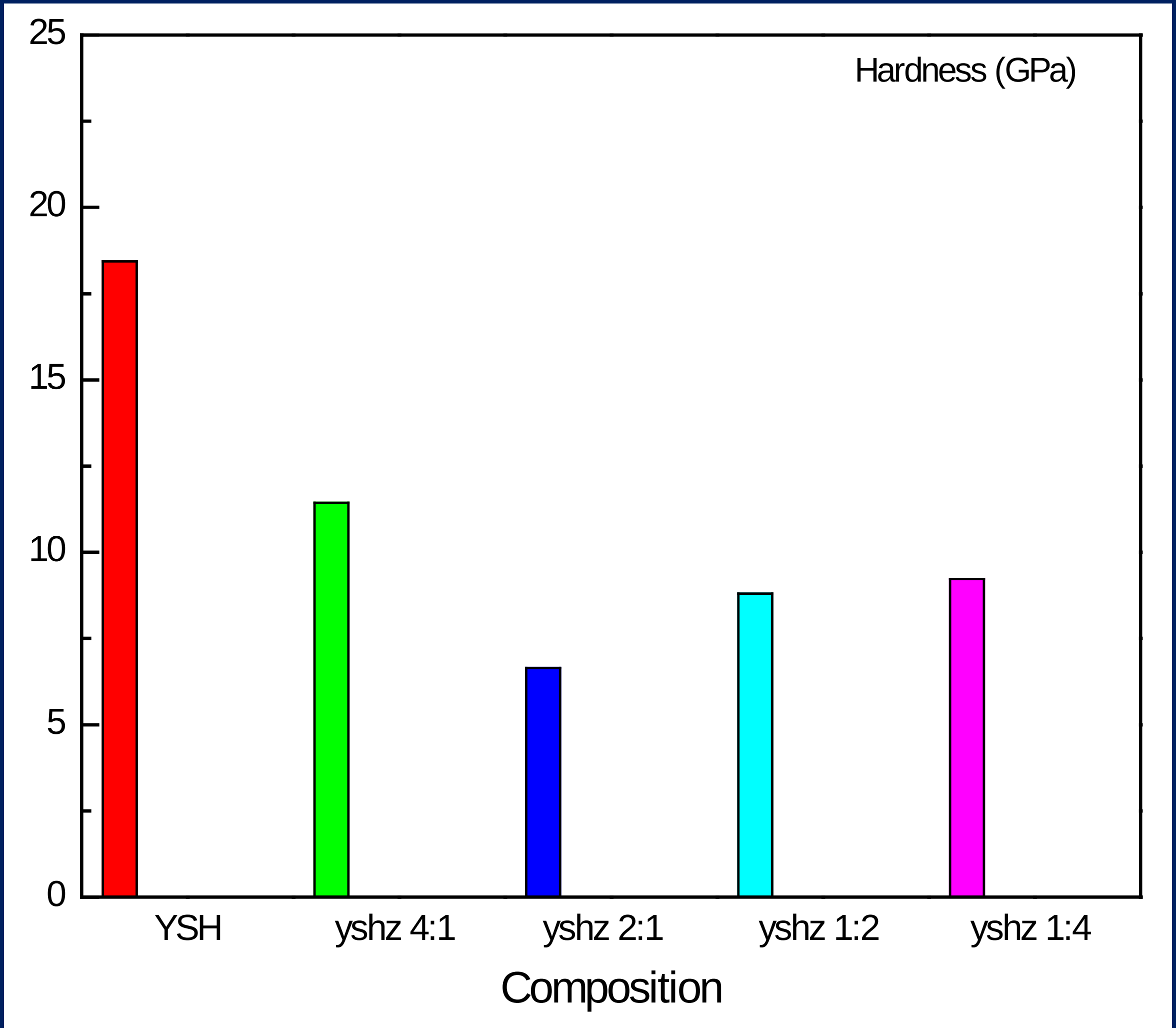
Thermal Phase Stability - YSHZ

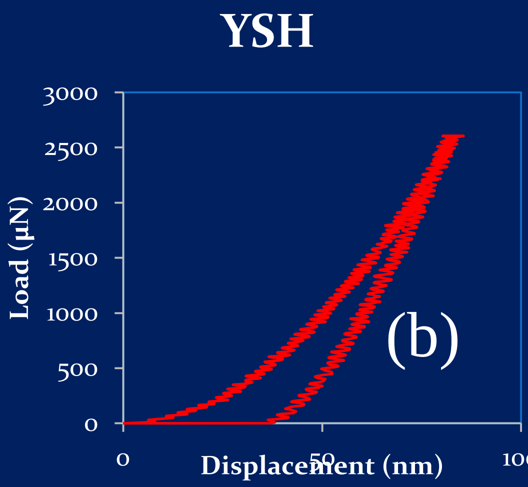


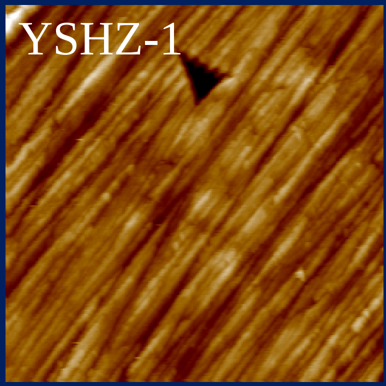


M. Noor-A-Alam et al., *Surf. Coat. Technol.* 206 (2011) 1628–1633

Mechanical Properties - YSHZ

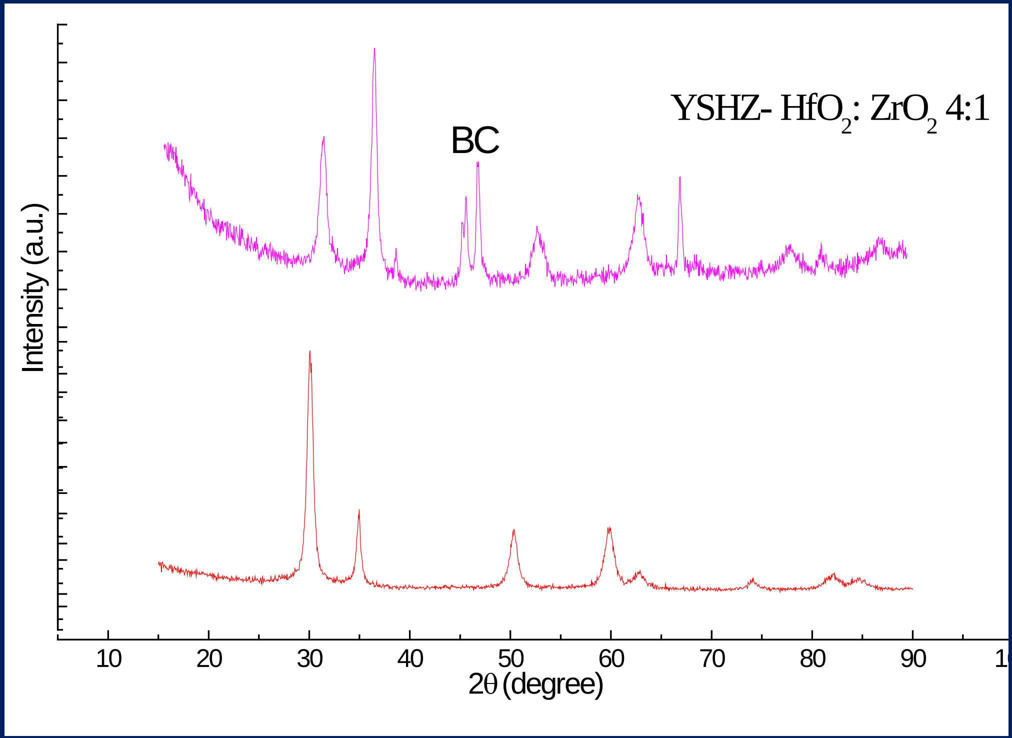


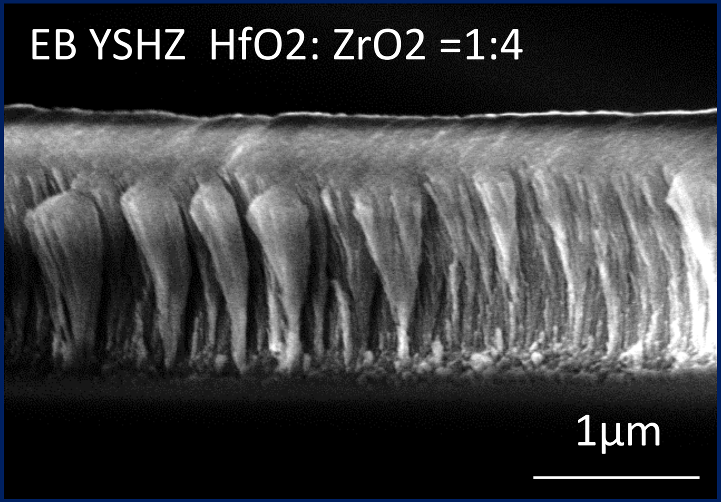




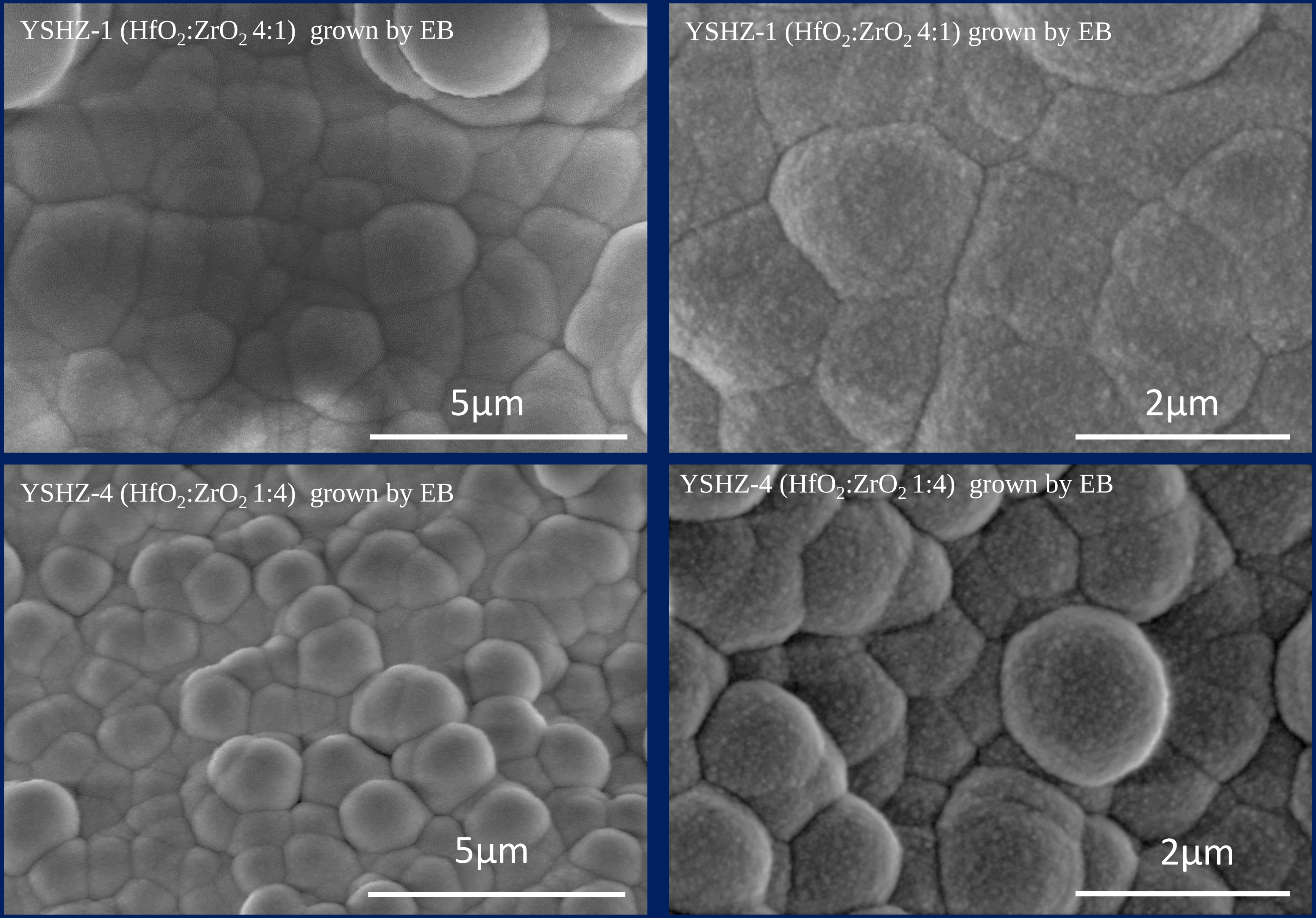
(c)

EBPVD YSHZ

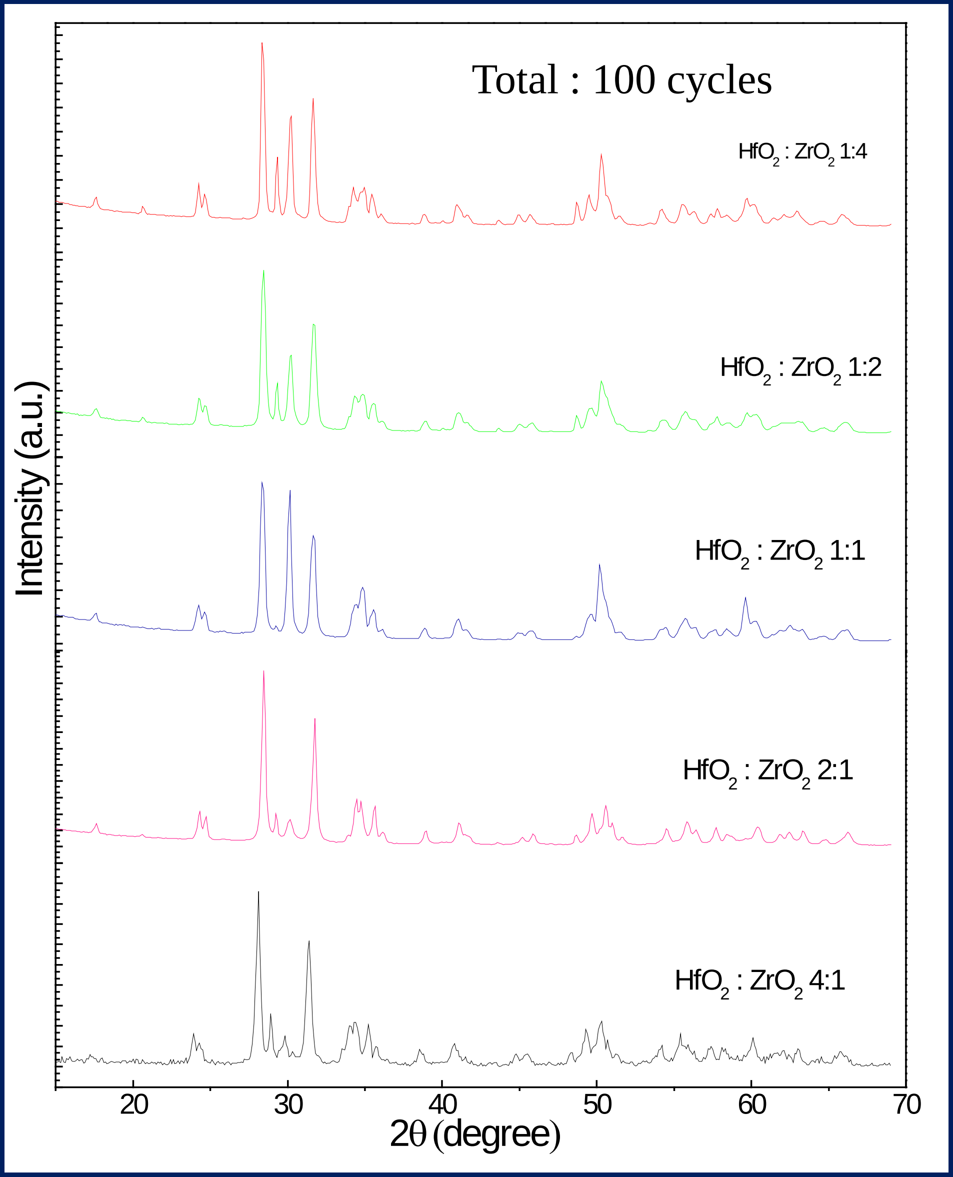

YSHZ- HfO_2: ZrO_2 4:1
BC
Intensity (a.u.)
10
20
30
40
50
60
70
80
90
2θ (degree)


EB YSHZ HfO2: ZrO2 =1:4
1μm

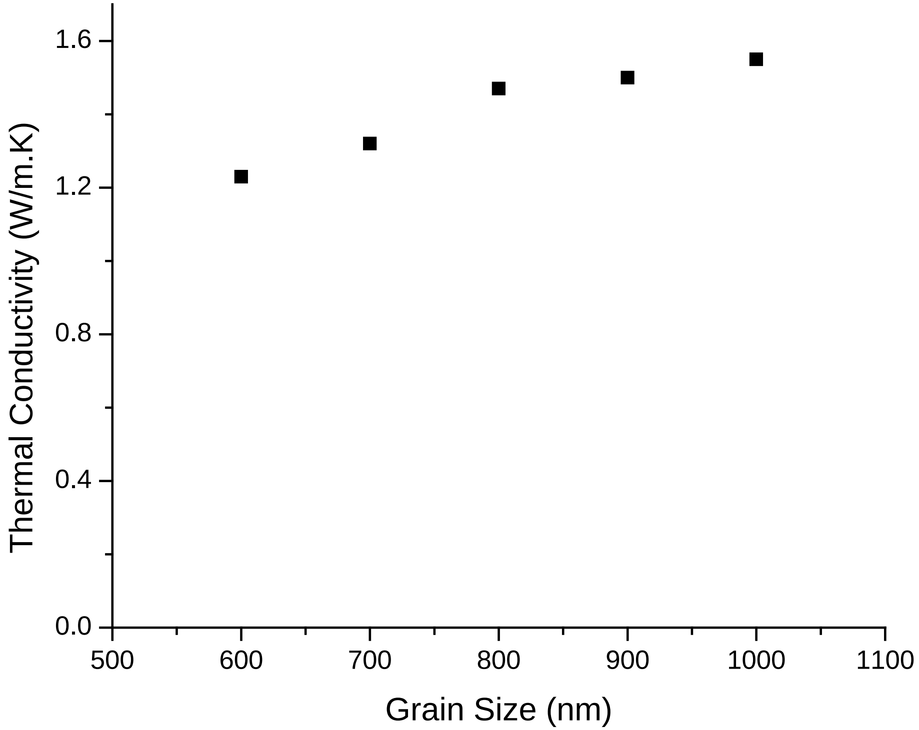
EBPVD YSHZ

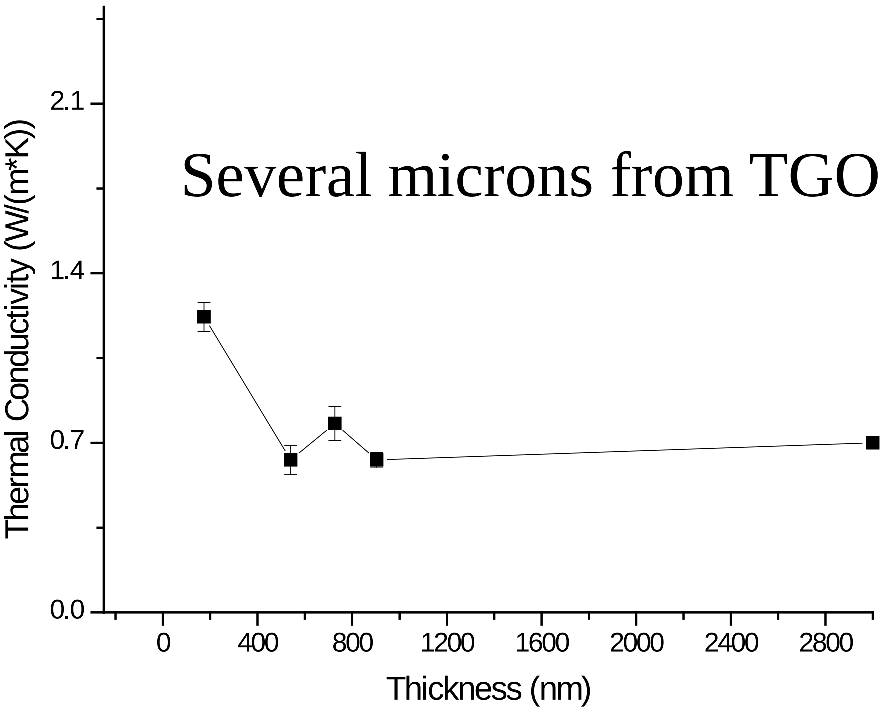

YSHZ-1 (HfO_2:ZrO_2 4:1) grown by EB
5μm
YSHZ-1 (HfO_2:ZrO_2 4:1) grown by EB
2μm
YSHZ-4 (HfO_2:ZrO_2 1:4) grown by EB
5μm
YSHZ-4 (HfO_2:ZrO_2 1:4) grown by EB
2μm

YSHZ – Thermal Cycling

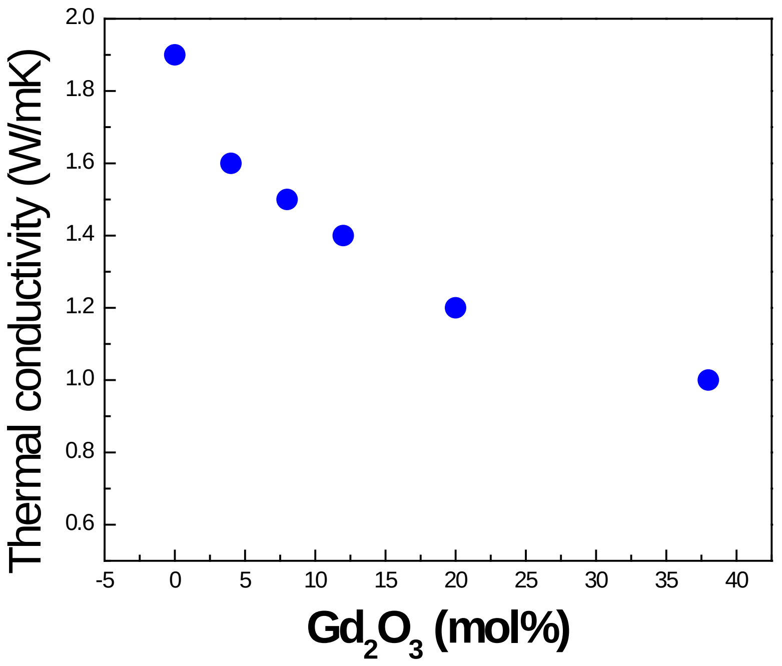


Thermal Conductivity - YSH

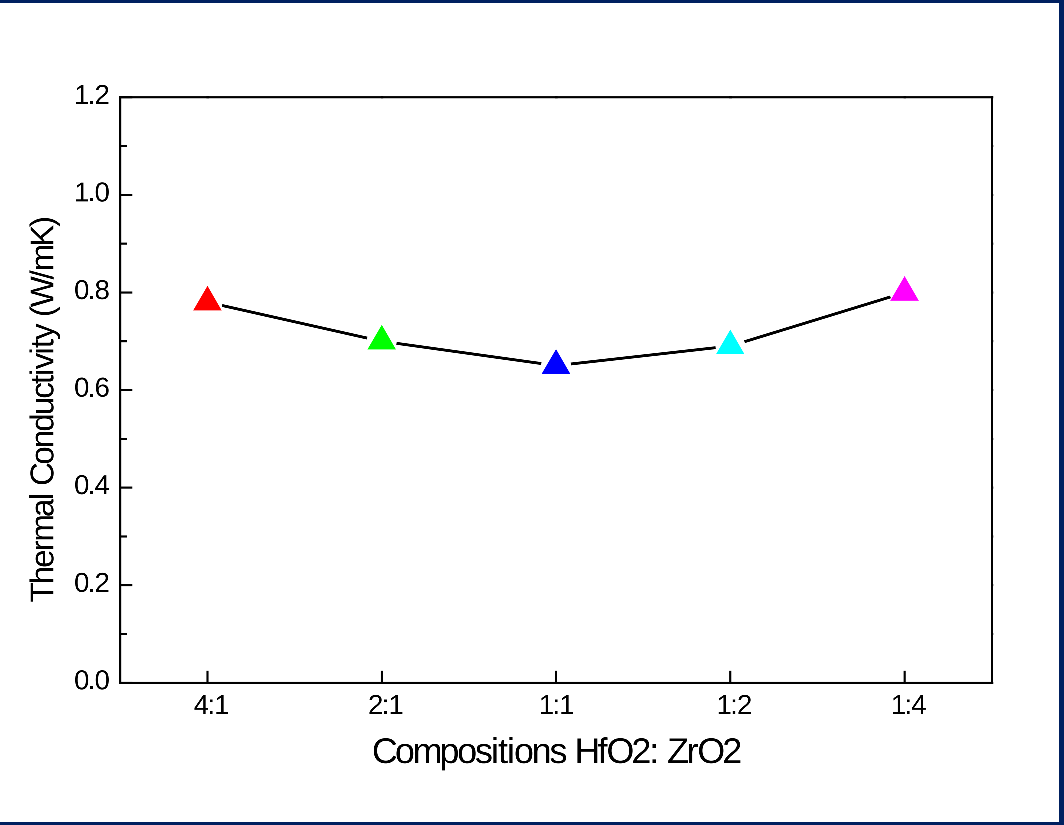




Thermal Conductivity -GSH



Thermal Conductivity - YSHZ



Mechanism

Extremely short
phonon mean free path

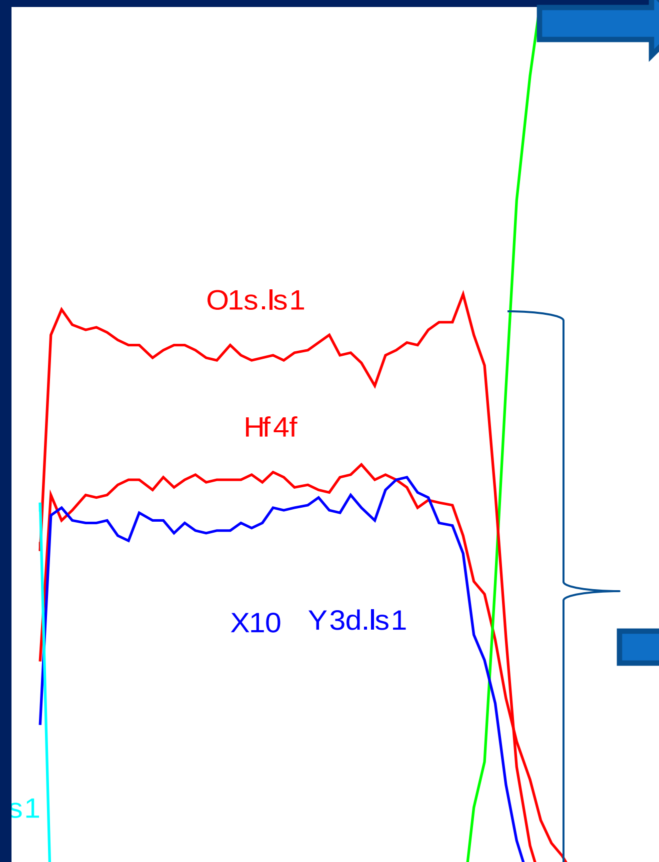
The effect is attributed to the mass disorder on the cation sublattice of ziconia in which Zr^{4+} ions are replaced with Hf^{4+}, decreasing the phonon mean free path

M. R. Winter and D. R. Clarke, *Acta. Mater.* 54 (2006) 5051

XPS

Data

Ion Etching

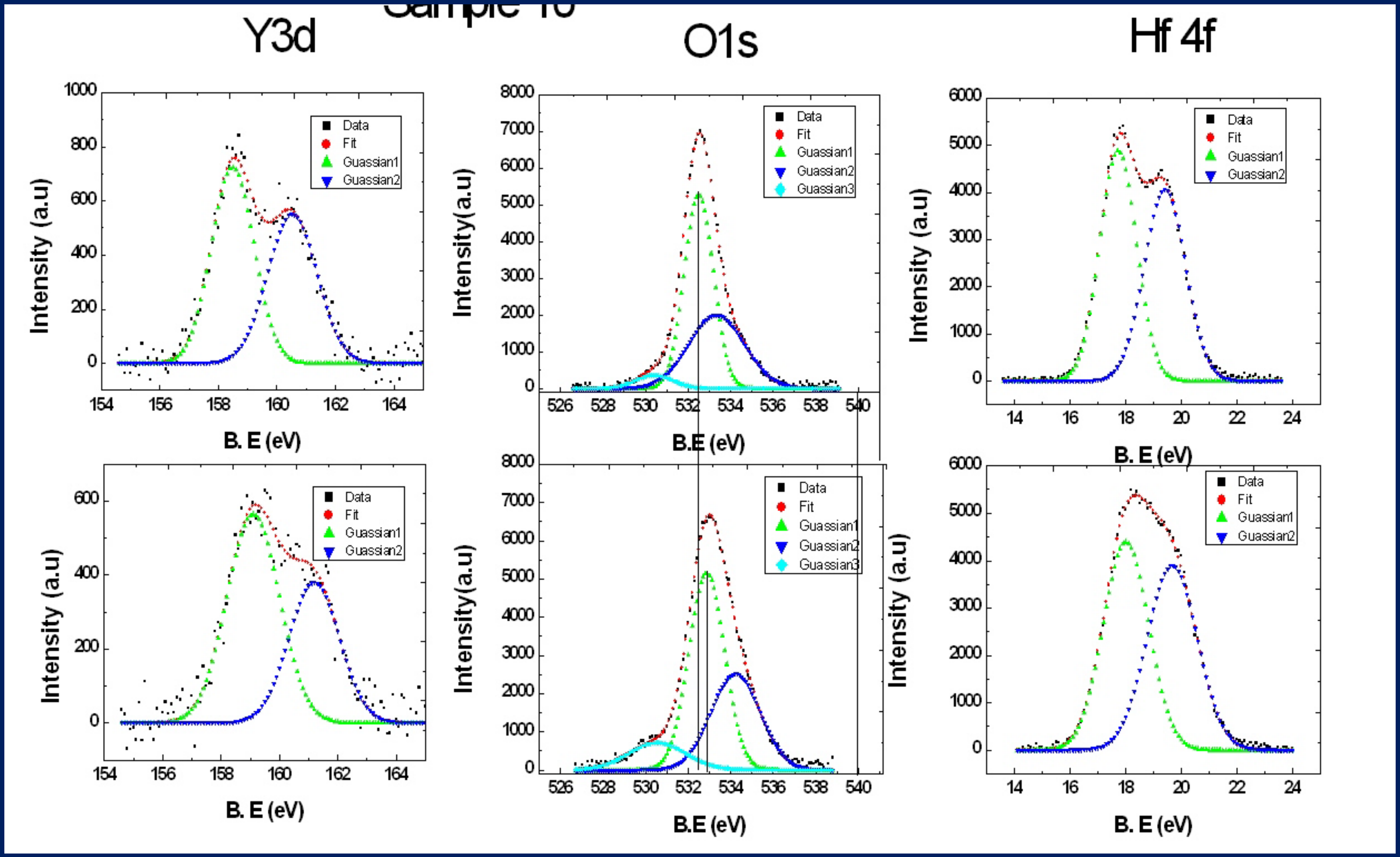


Substrate

Y^{3+} and Hf^{4+}

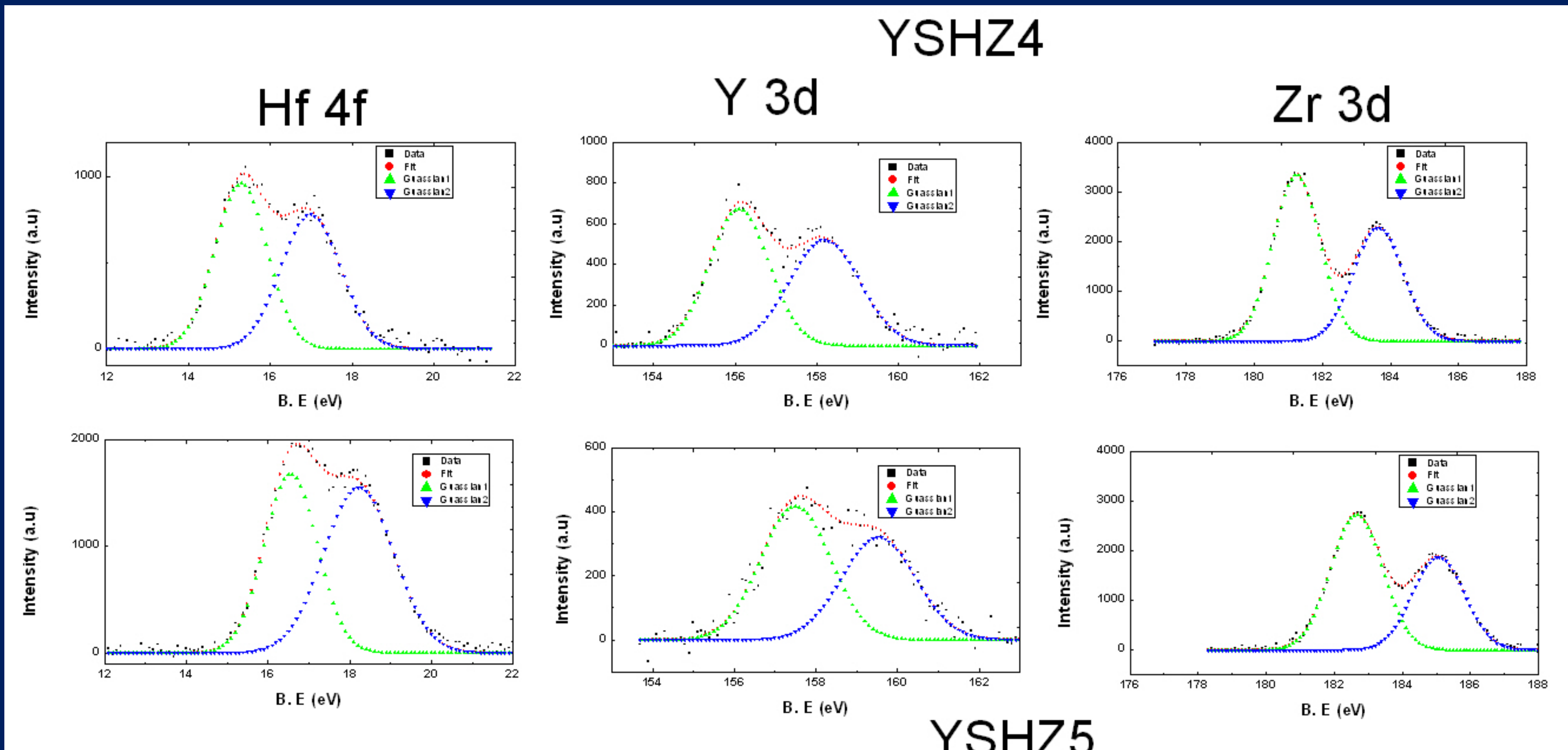
O, Y and Hf
From Coating

XPS

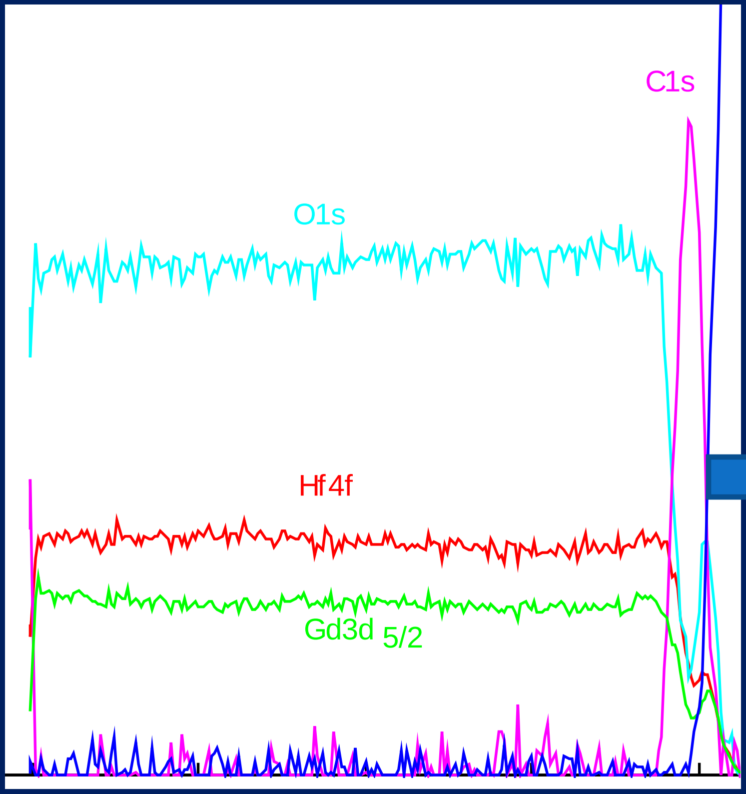


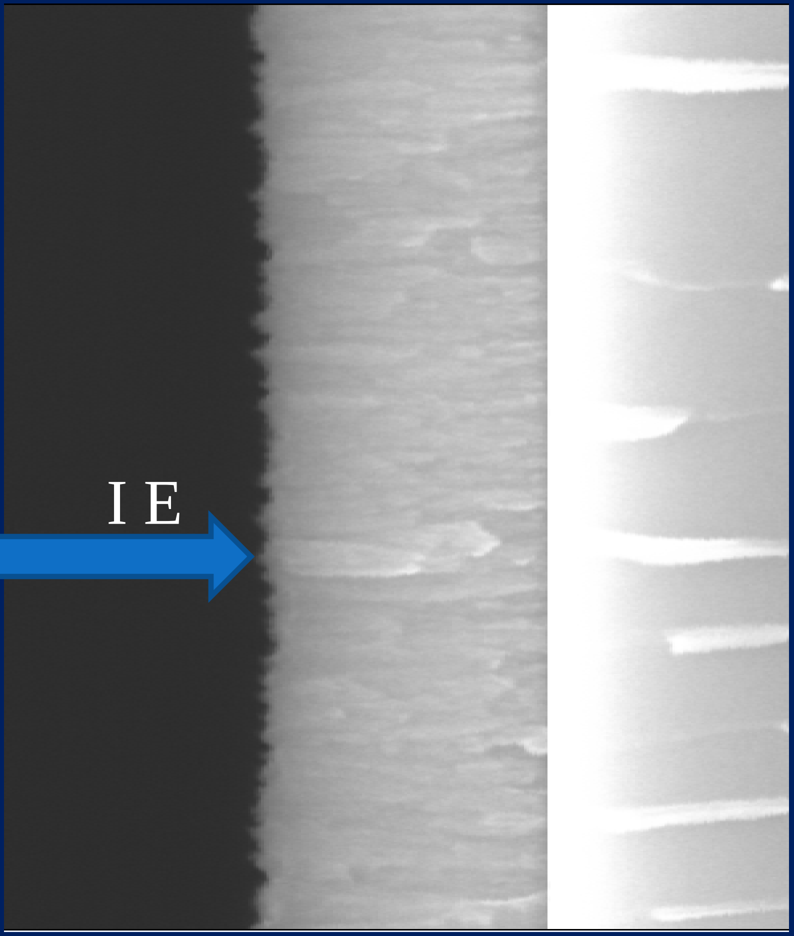
Y3d
O1s
Hf 4f
Data
Fit
Guassian1
Guassian2
Guassian3
Intensity (a.u)
Intensity(a.u)
B. E (eV)
B.E (eV)

XPS



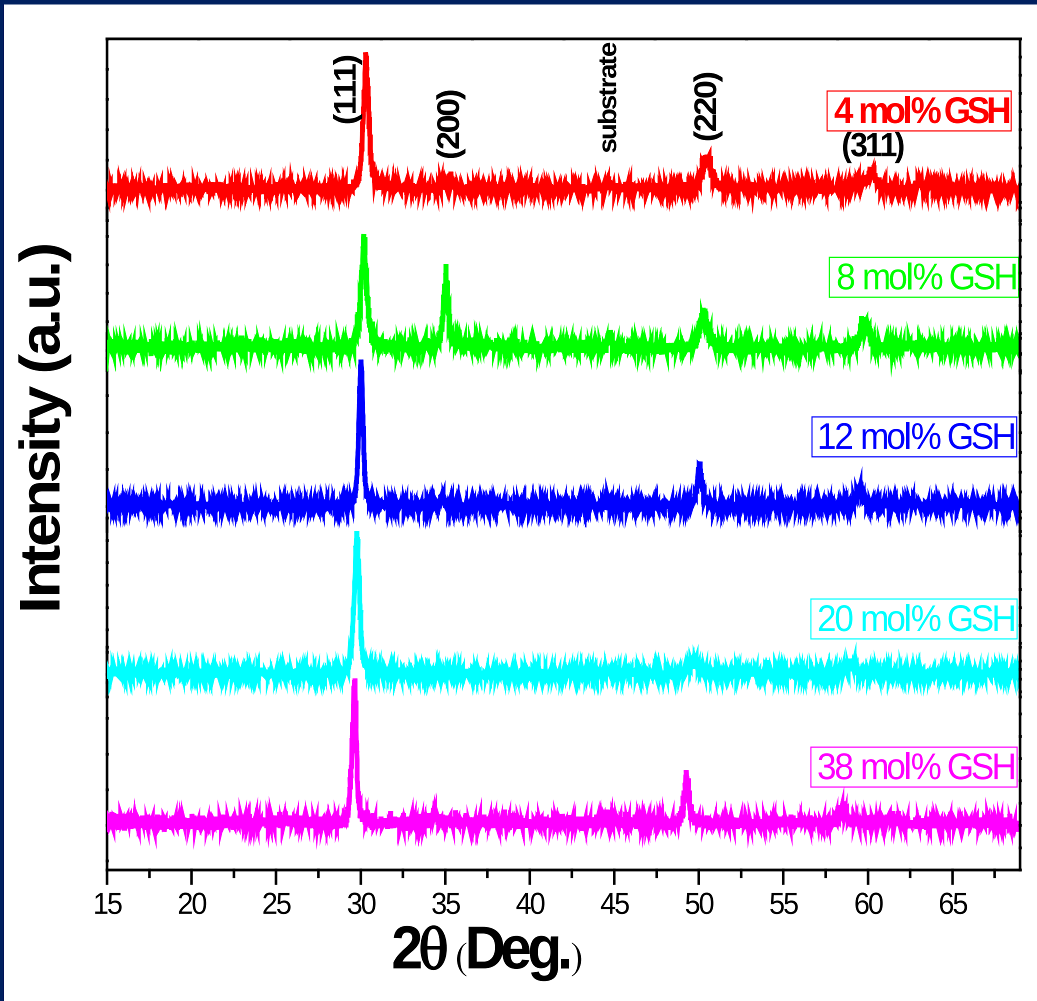
XPS

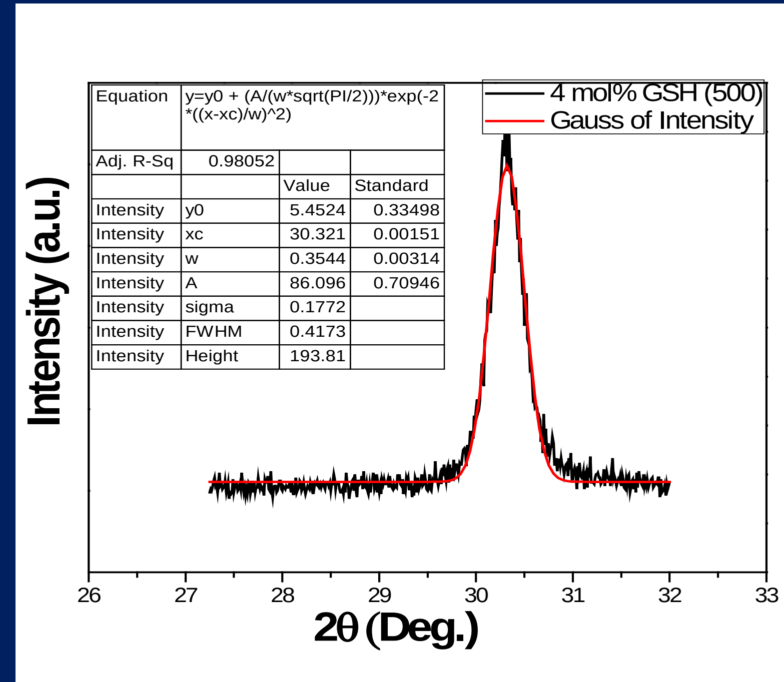


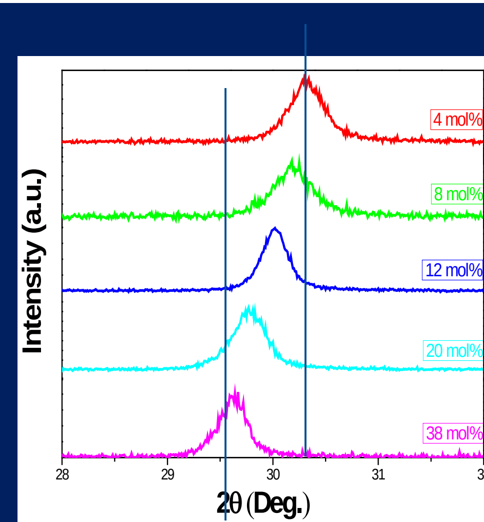


GSH

Structure and Phase

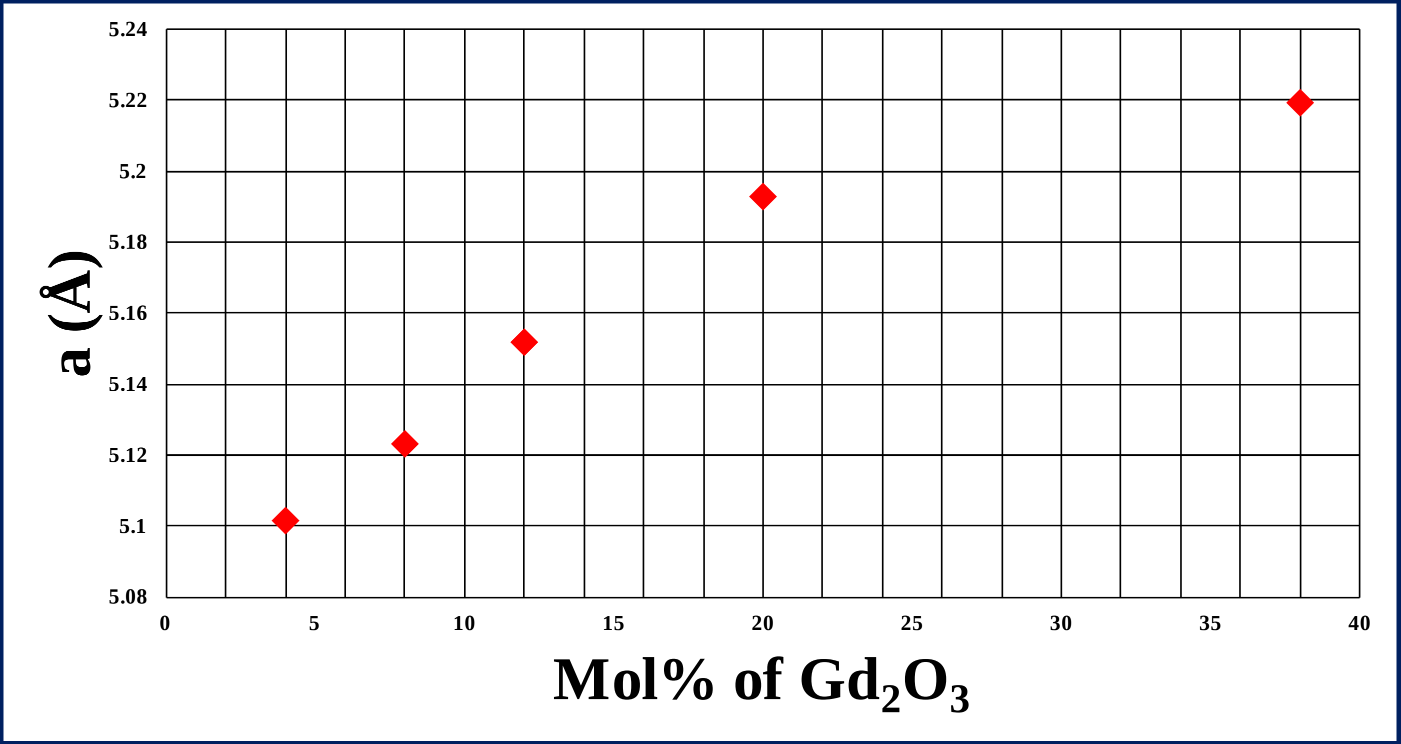






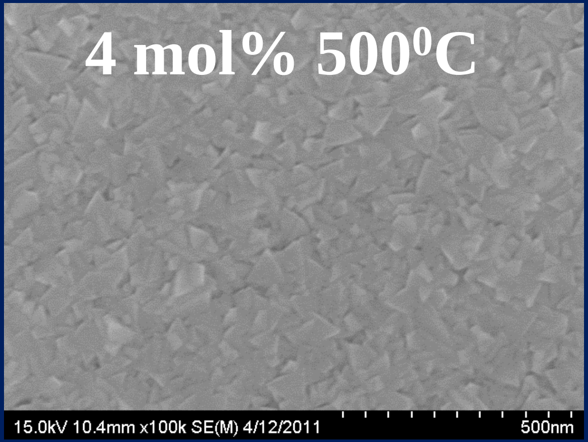
C.K. Roy, M. Noor-A-Alam , A.R. Choudhuri and C.V. Ramana, *Ceram. Inter.* 206 (2011) 1628–1633

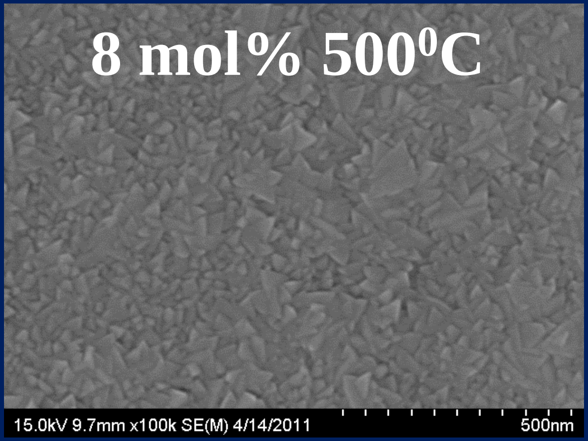
Effect of Gd_2O_3 Composition

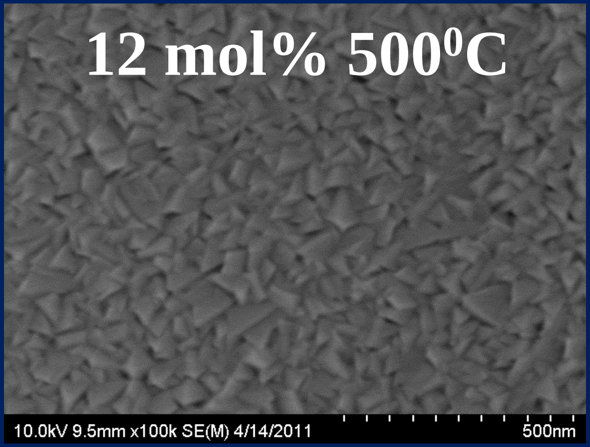


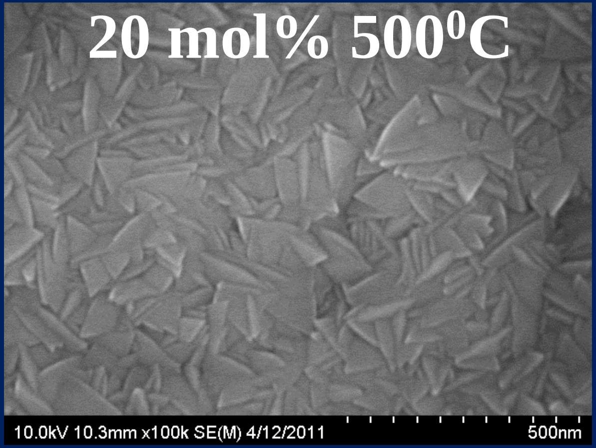
Increasing Gd_2O_3 increases the lattice constant; stiffens the lattice leading to slightly higher values of hardness of the coatings

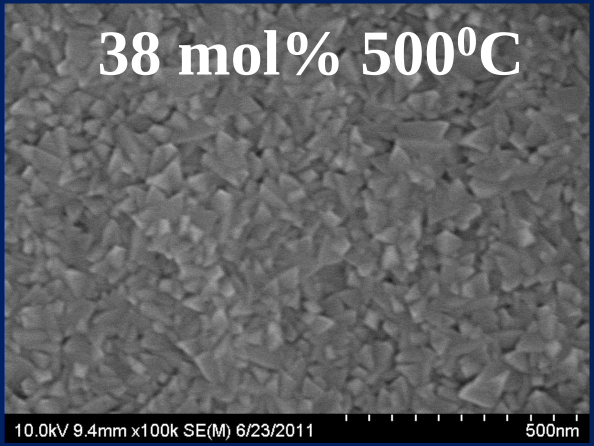
Effect of Gd_2O_3 Composition - Morphology



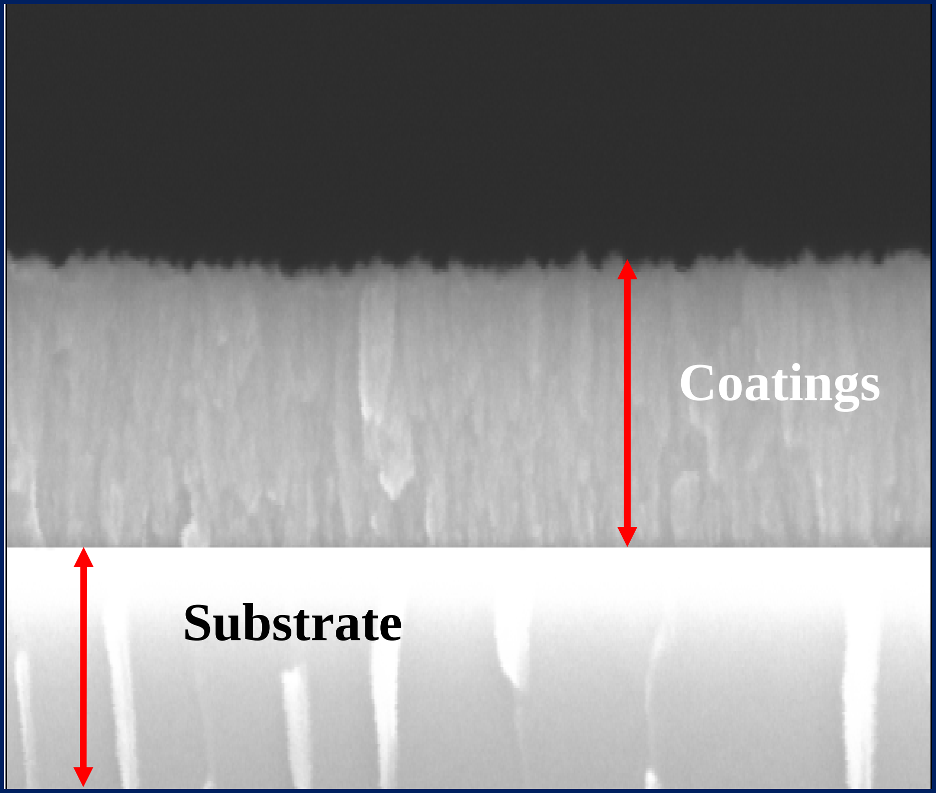


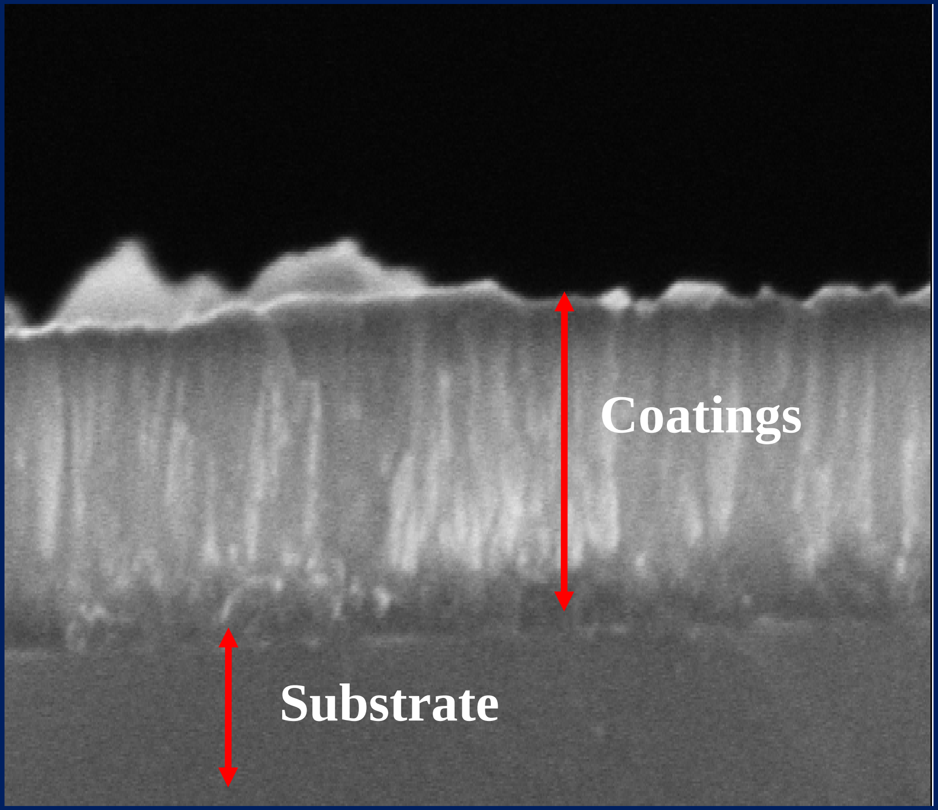




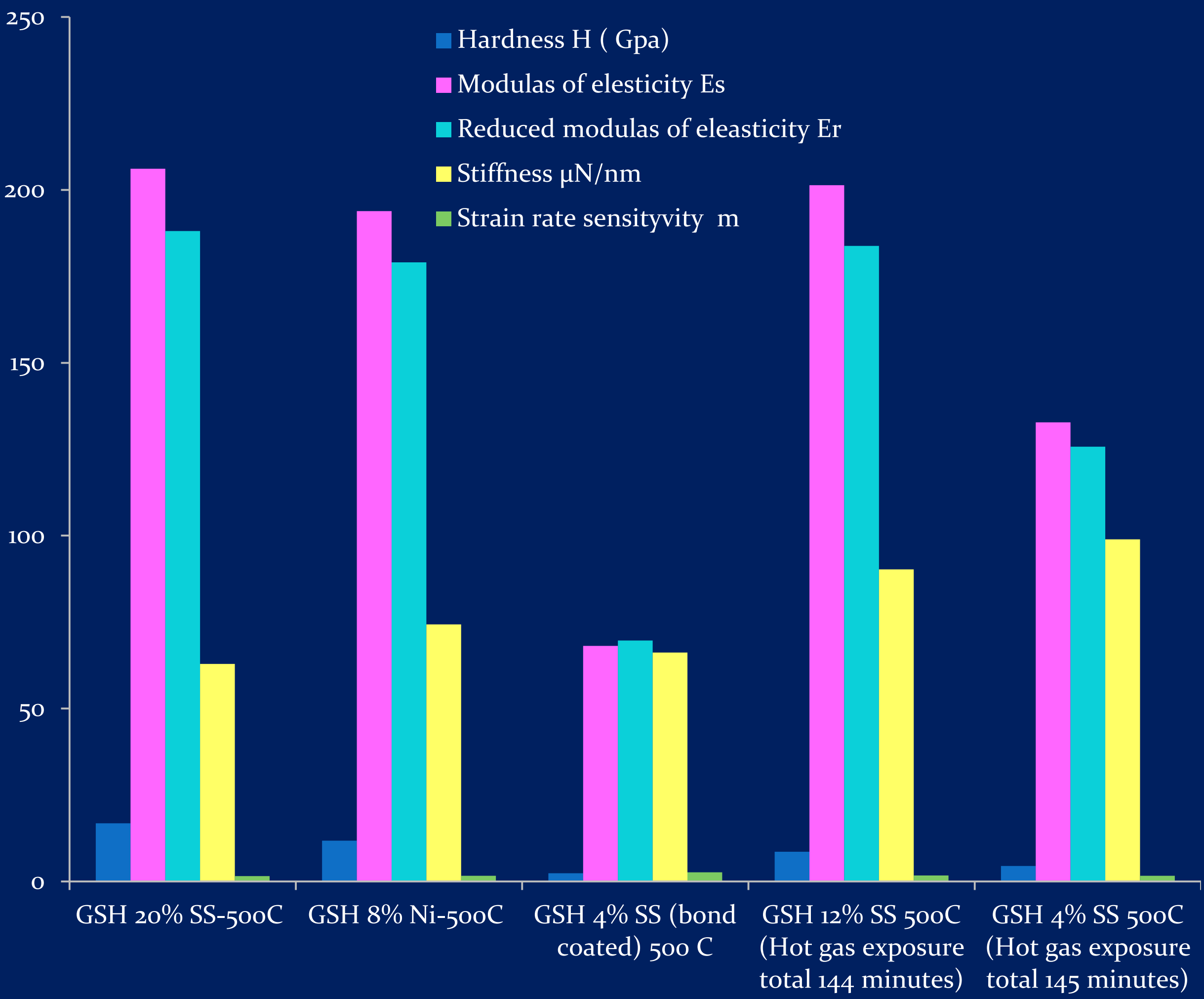


Effect of Gd_2O_3 Composition

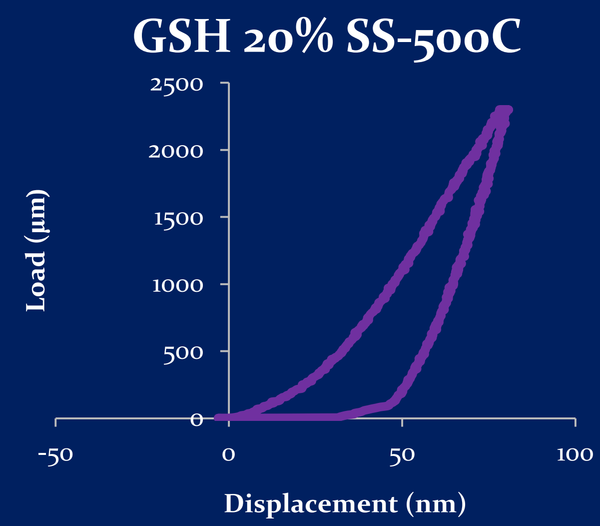




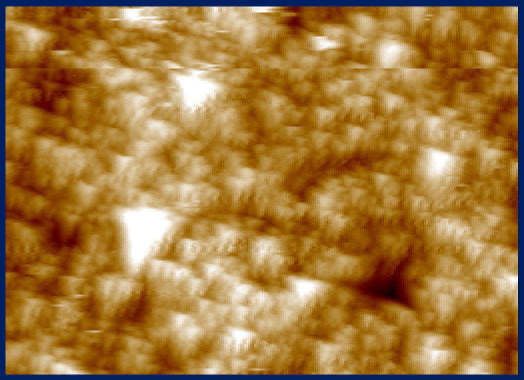
Mechanical Properties - GSH



(a)



(b)



GSH 12% SS 500C (Hot gas exposure total 144 minutes)

(c)

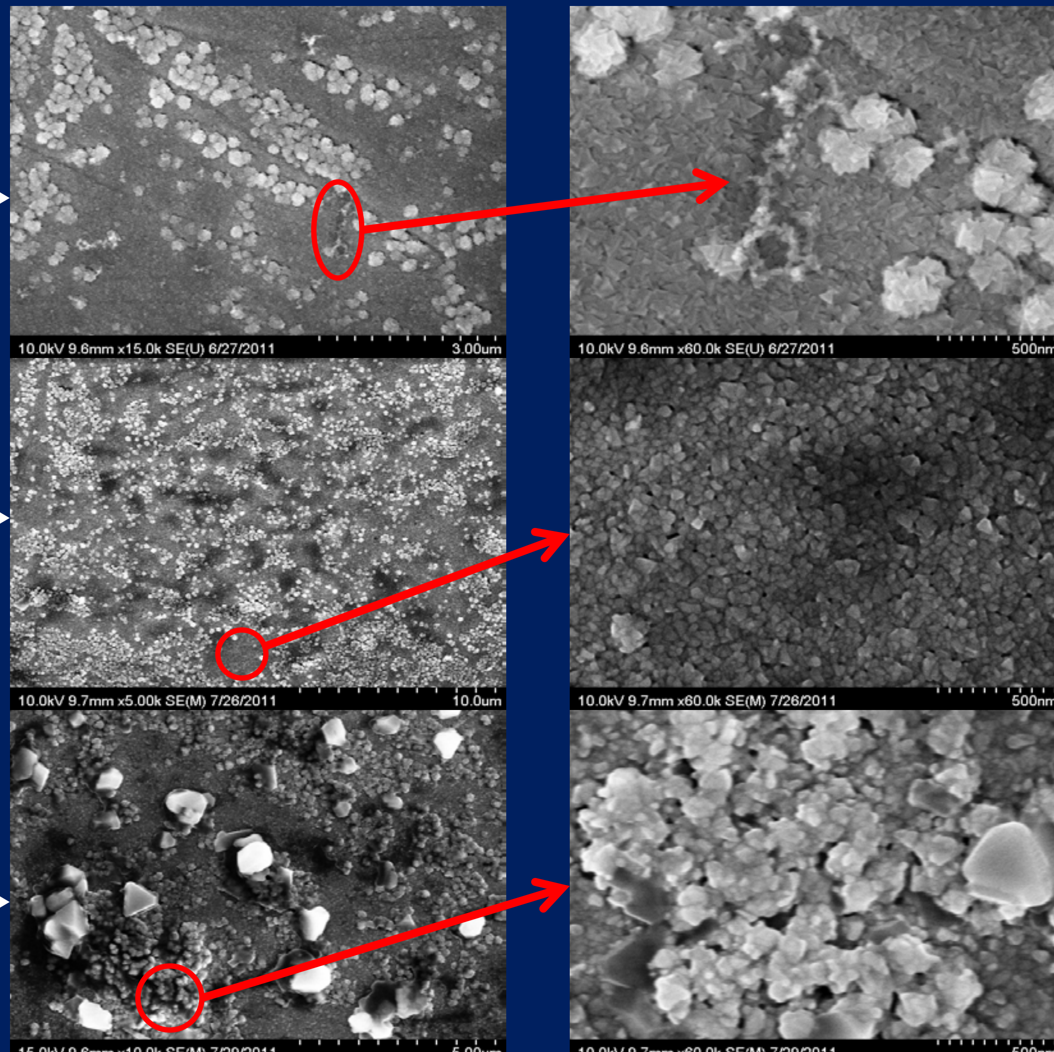
Hot Gas Exposure

4 mol%, impingement angle 90°

After test 1
(5 minutes)

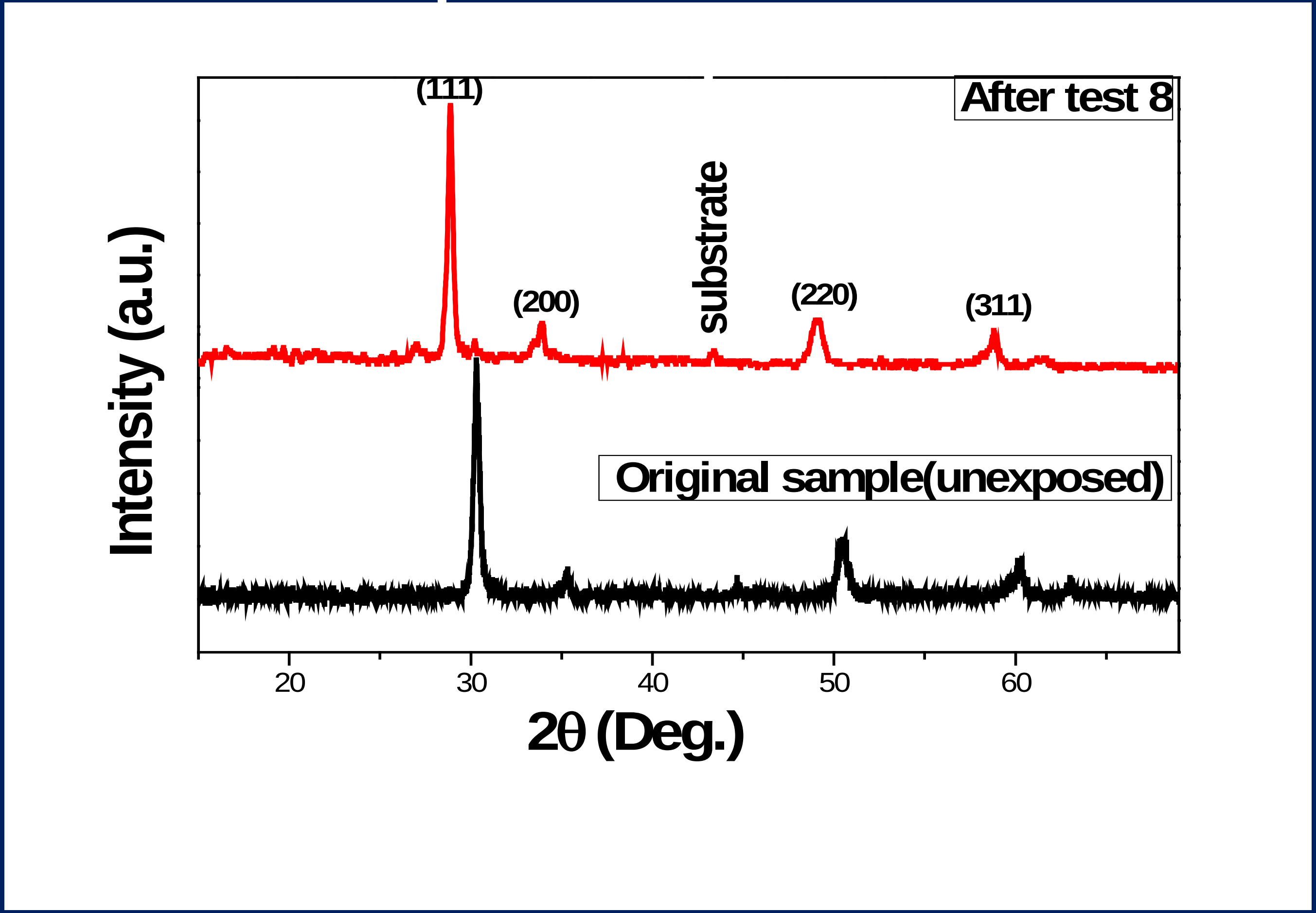
After test 5
(80 minutes)

After test 8
(145 minutes)



Hot Gas Exposure

XRD patterns of 4 mol% GSH



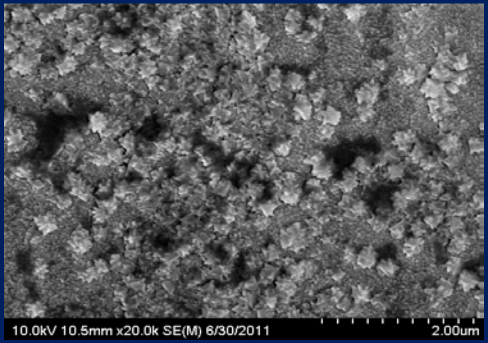
Peak shift (30.32 ° - 28.87 °)= 1.45°

Lattice constant increased by (5.35 Å - 5.150Å)= 0.25 Å

12 mol%, impingement angle 90^0

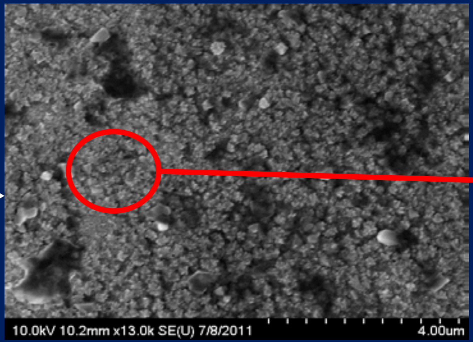
After Test 3

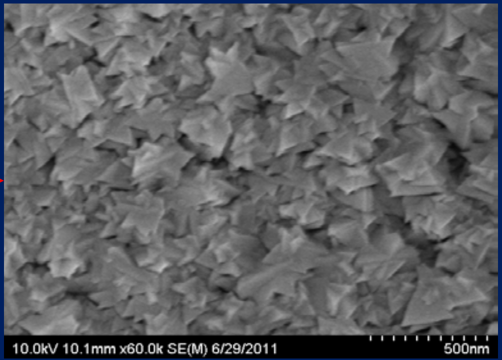
(45 minutes)



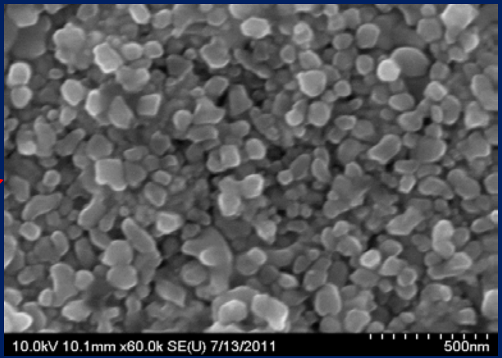
After Test 5

(85 minutes)

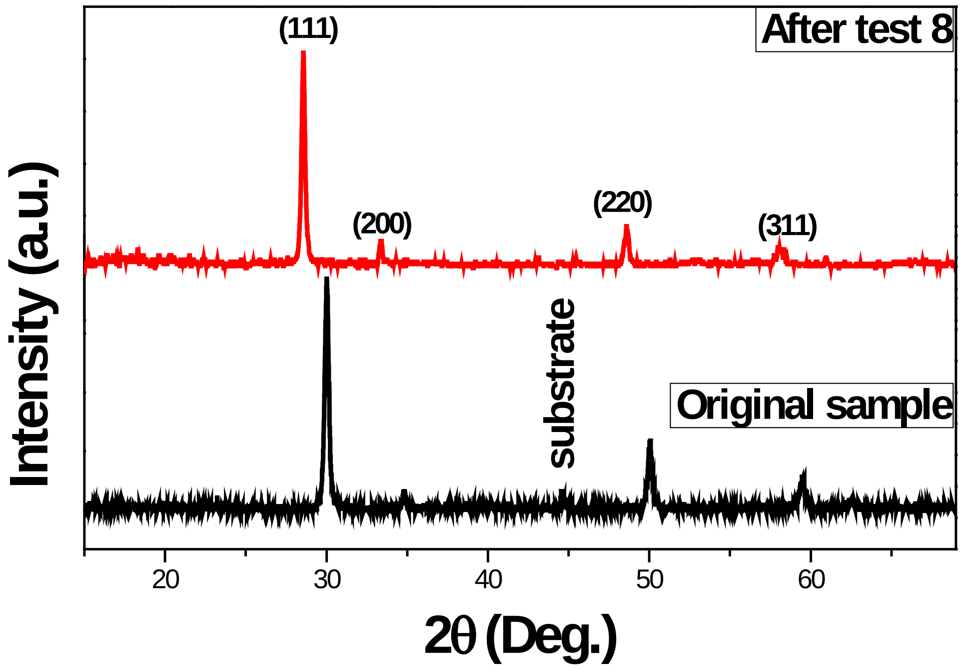




After Test 8
(144 minutes)



XRD patterns of 12 mol% GSH after exposure



Peak shift (30.02 ° - 28.57 °)= 1.45

Lattice constant increased by (5.40 Å - 5.15 Å)= 0.25 Å

AET

Summary and Conclusions

- Hafnia-based coatings were grown and their microstructure and phase/compositional stability is studied
- Columnar structure is seen in all the coatings; however, the Gd_2O_3 content influences the "size" in GSH coatings
- YSH and YSHZ coatings exhibit the cubic phase, which is stable to higher temperatures; GSH coatings exhibit either cubic or pyrochlore structure depending on Gd_2O_3 content
- Lattice expansion and mechanical property evaluation indicates there is a limit to play with the Hf-Zr-O composition (i.e., HfO_2 vs. ZrO_2 ratio in the matrix)
- Thermal conductivity and hot gas exposure studied indicating that there are compositions in YSZH and GSH that are promising with effective reduction

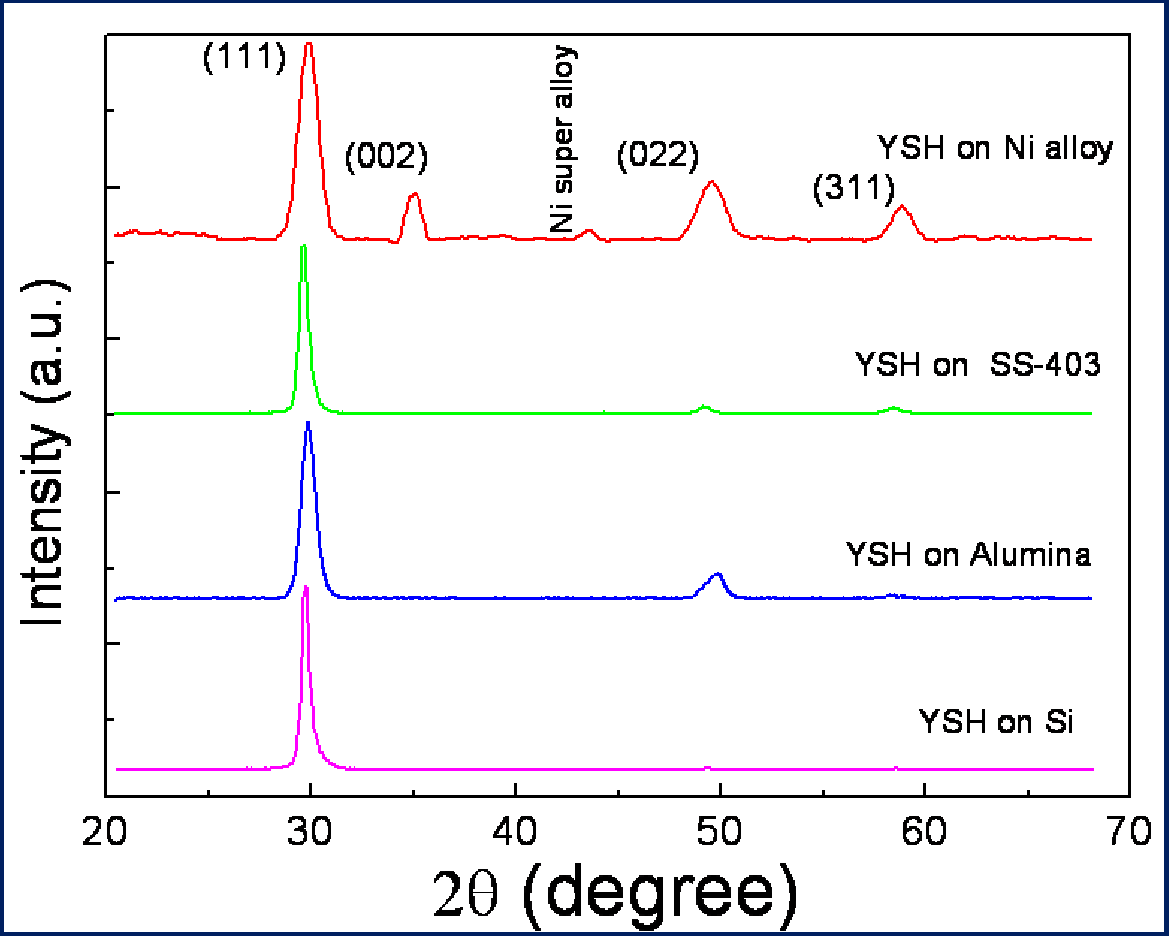
Acknowledgements

- DOE
- Dr. Briggs White
- cSETR
- M. Noor-A-Alam, Satya K. Gullapalli, Chandan K. Roy, Ernesto Rubio & Chris Bradley
- PNNL (Drs. Thevuthasan and Mark Engelhard)

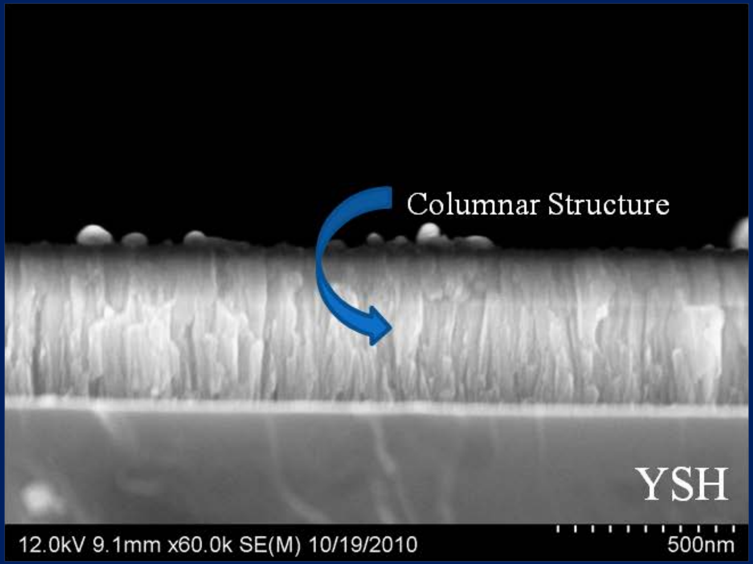
THANK YOU!

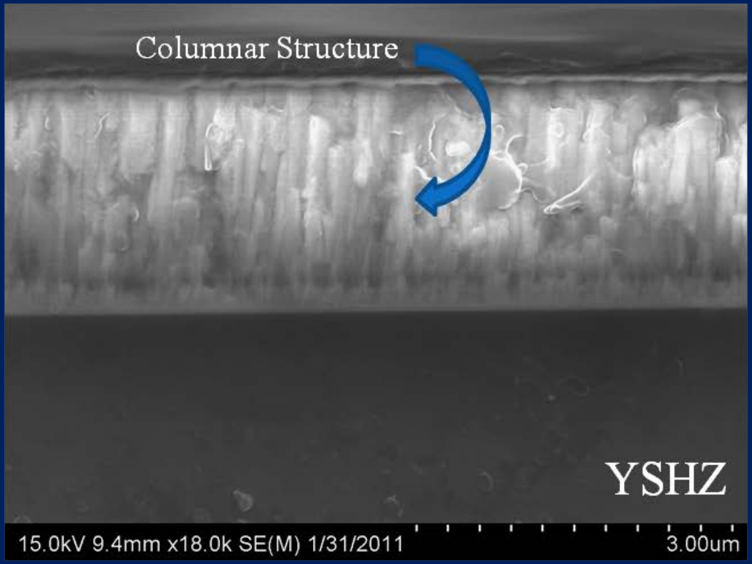
QUESTIONS/
COMMENTS?

YSH - Effect of Substrate Material

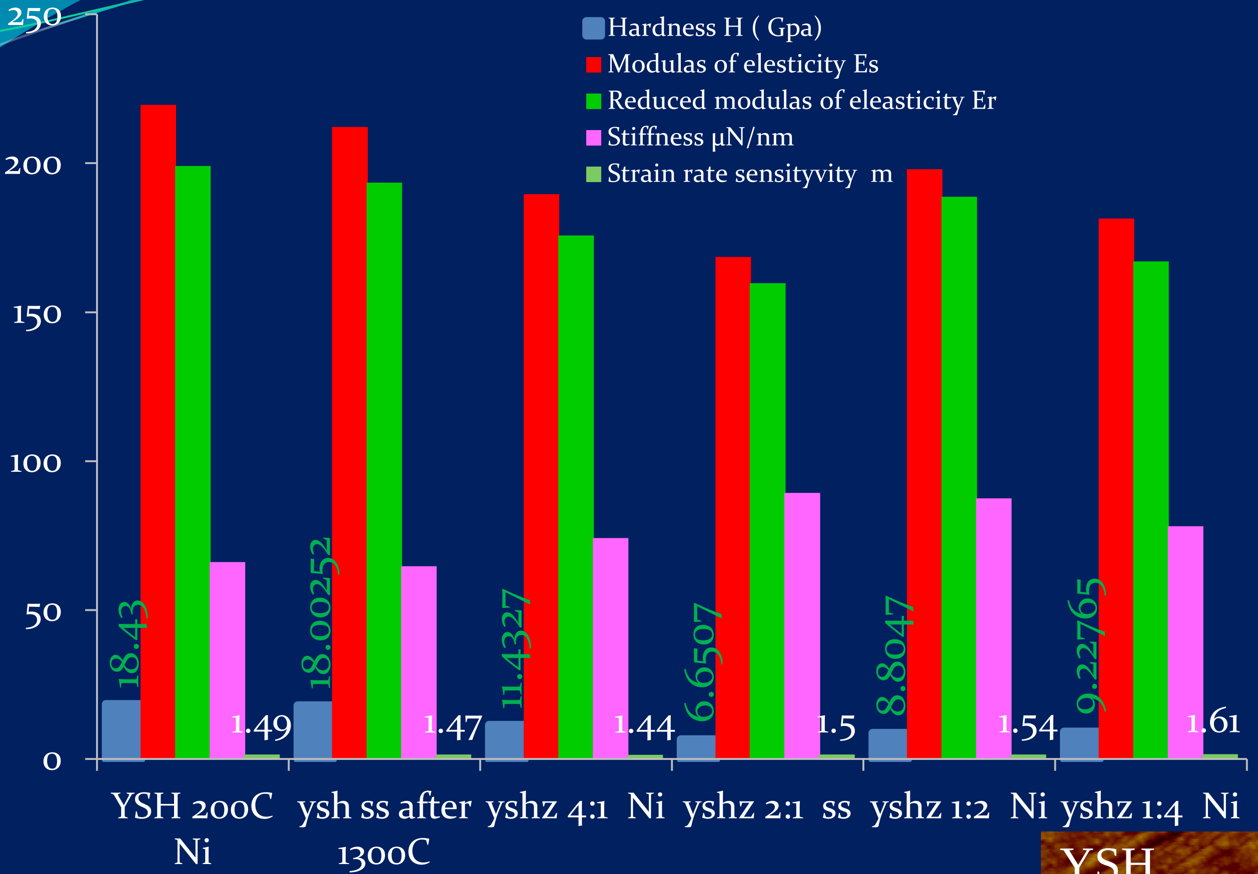


Columnar Structure:

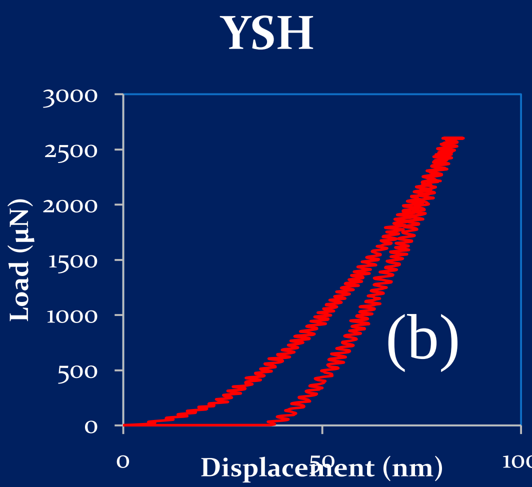




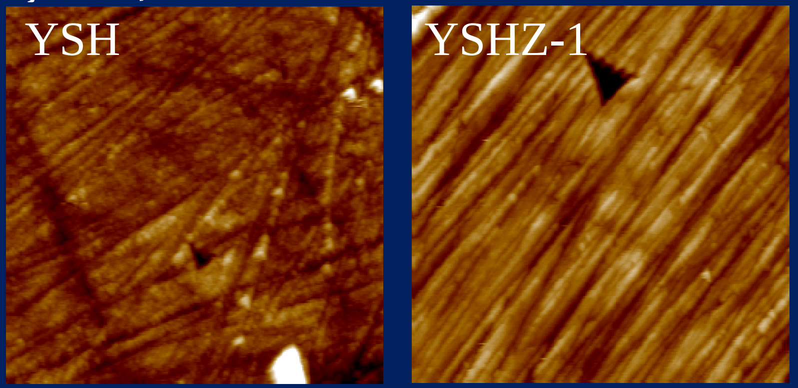
Mechanical Properties - YSHZ



(a)



(b)



(c)

Optical measurement of YSH on alumina