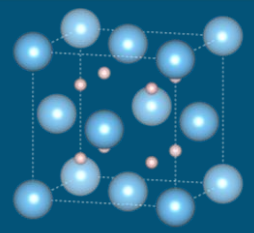
SAND2024-02415C

Sandia National Laboratories

Characterization of δ-TiHx powders: A synergistic application of XRD, LIBS, and QCM methods



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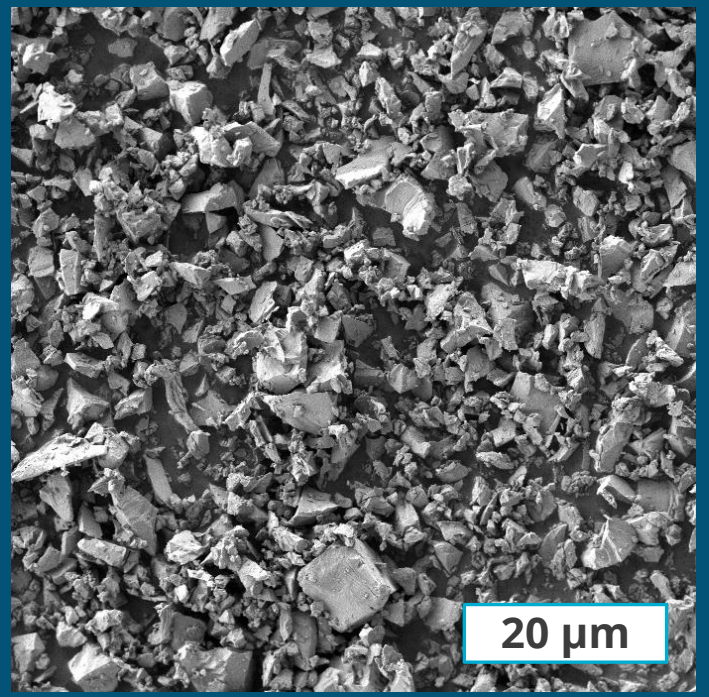
Titanium hydride applications

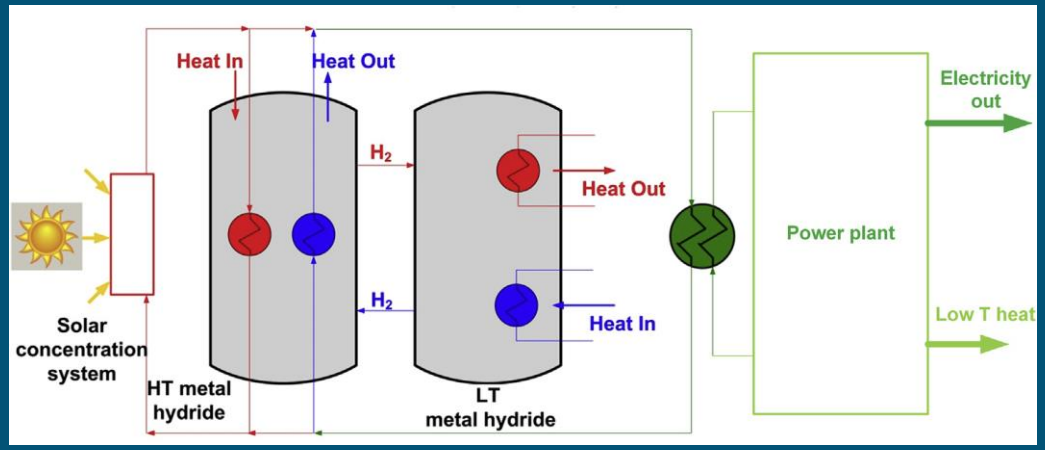
- Intermediate in HDH Ti powder production
- Blowing agent for metal foam
- Powder metallurgy and additive manufacturing
  - Novel oxide reduction agent
- Hydrogen storage
  - Energy applications
  - Release of high-purity hydrogen
- Model system
  - Similar concerns with other metal hydrides

Need for precision hydrogen quantitation in hydrogen-rich (up to several wt. %) materials ($TiH_{x.xx}$)



TiH_2 powder

Via Wikimedia Commons , user Stehfun



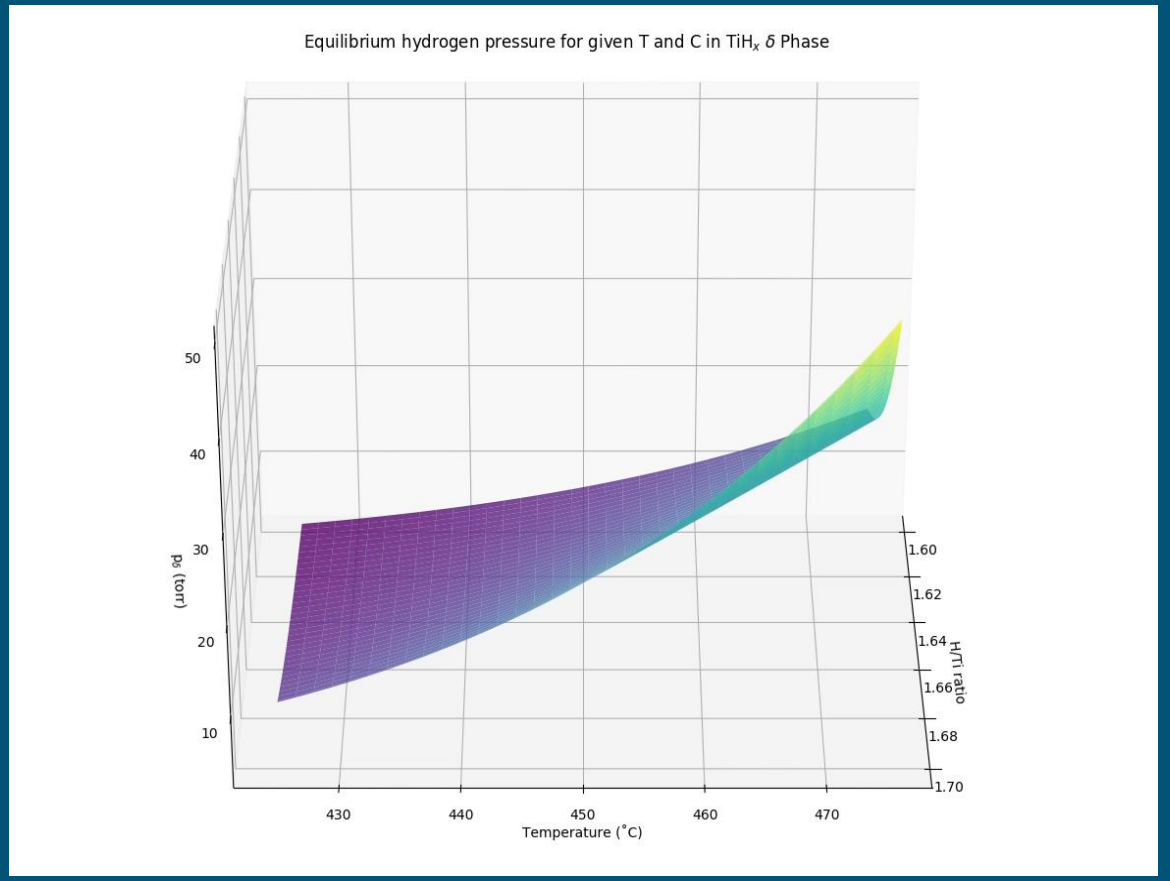
Corgnale, et al, Int J Hydrogen Energy 2016

Equilibrium approach to composition control

- Control δ-TiH_x hydrogen content by varying equilibrium state
  - Temperature and pressure uniquely dictate composition

Starting material (TiH_2) → **Heat** → Hold at prescribed T & P → **Cool** → Remove material ($TiH_{1.xx}$)

- Repeatable and tightly controlled compositions
  - Through precise control of temperature and pressure conditions in reactor
- Applicable to all spatial scales
  - Applied here to <44μm powders and >1mm pellets
  - Processing time varies due to diffusion kinetics

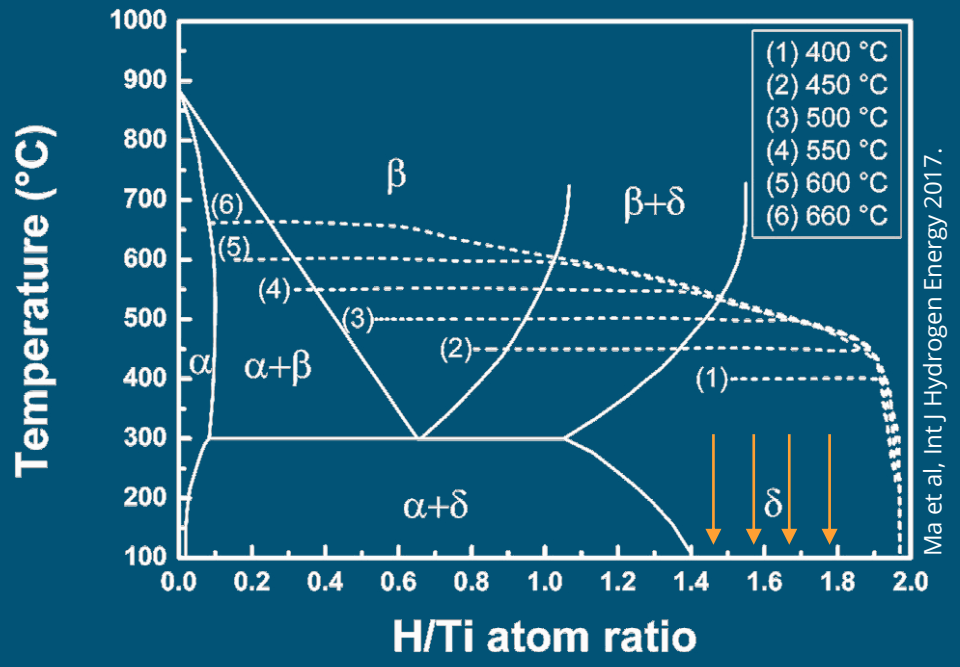


δ-TiH_x pressure-temperature-composition surface computed via the approach outlined in Wang, J Alloy Comp, 1996.

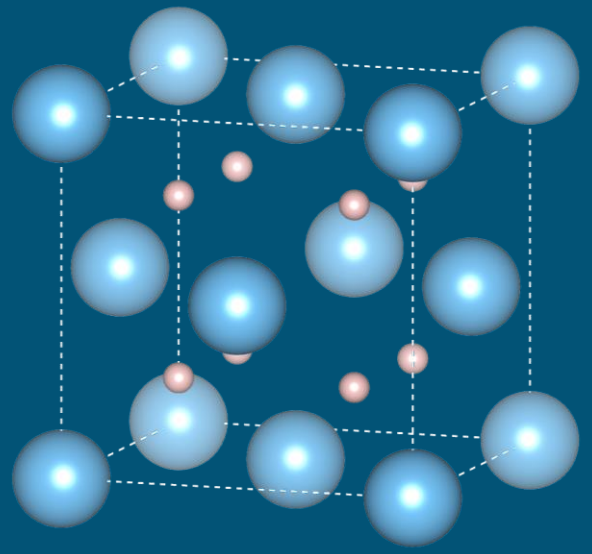
Hydrogen removal, addition, and compensation for variances in precursor composition and amount

H-Ti Phases

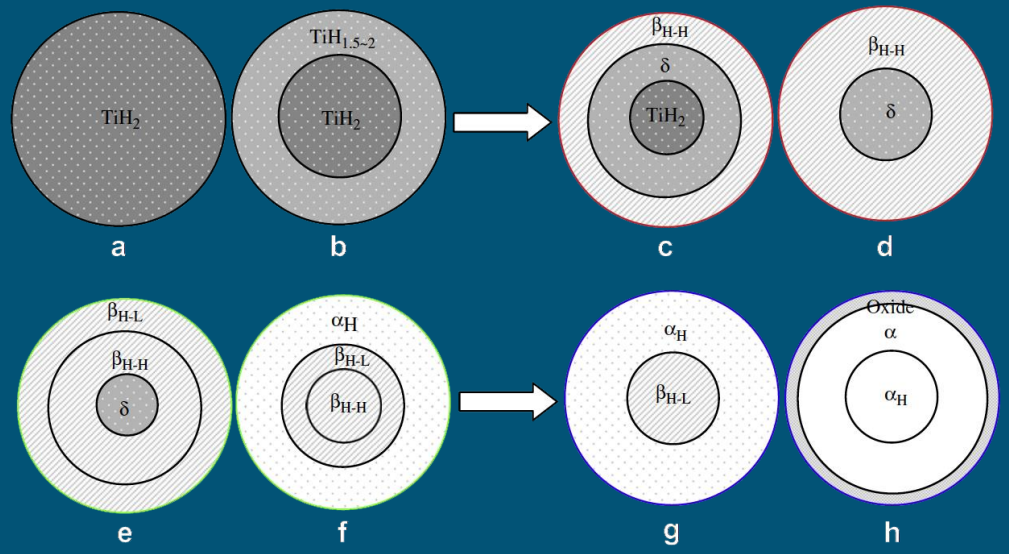
- Phases present: α-Ti, β-Ti, and δ-TiH_x
  - Coexistence of multiple phases
- Significant capacity to absorb oxygen
- Hydrogen release starting at 250 to 350 ˚C
- TiH_x remains in a single phase (δ) from x ≈ 1.5 to 2 at room temperature



Ma et al, Int J Hydrogen Energy 2017.



δ-TiH_2 Unit cell rendered in VESTA

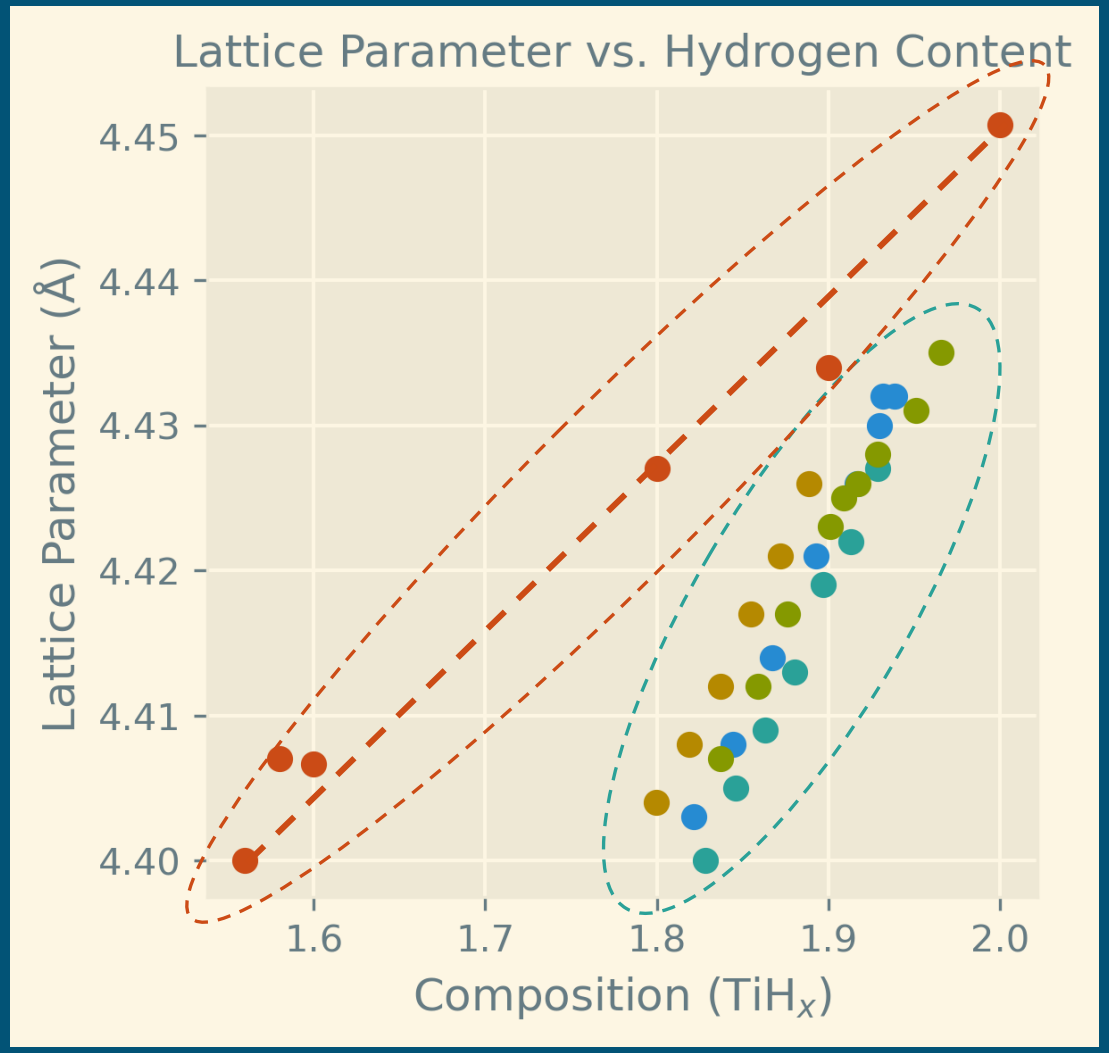


Wang et al, Int J Hydrogen Energy 2009.

Important to quantify phases present and hydrogen content

X-ray diffraction (XRD) for hydrogen content quantification

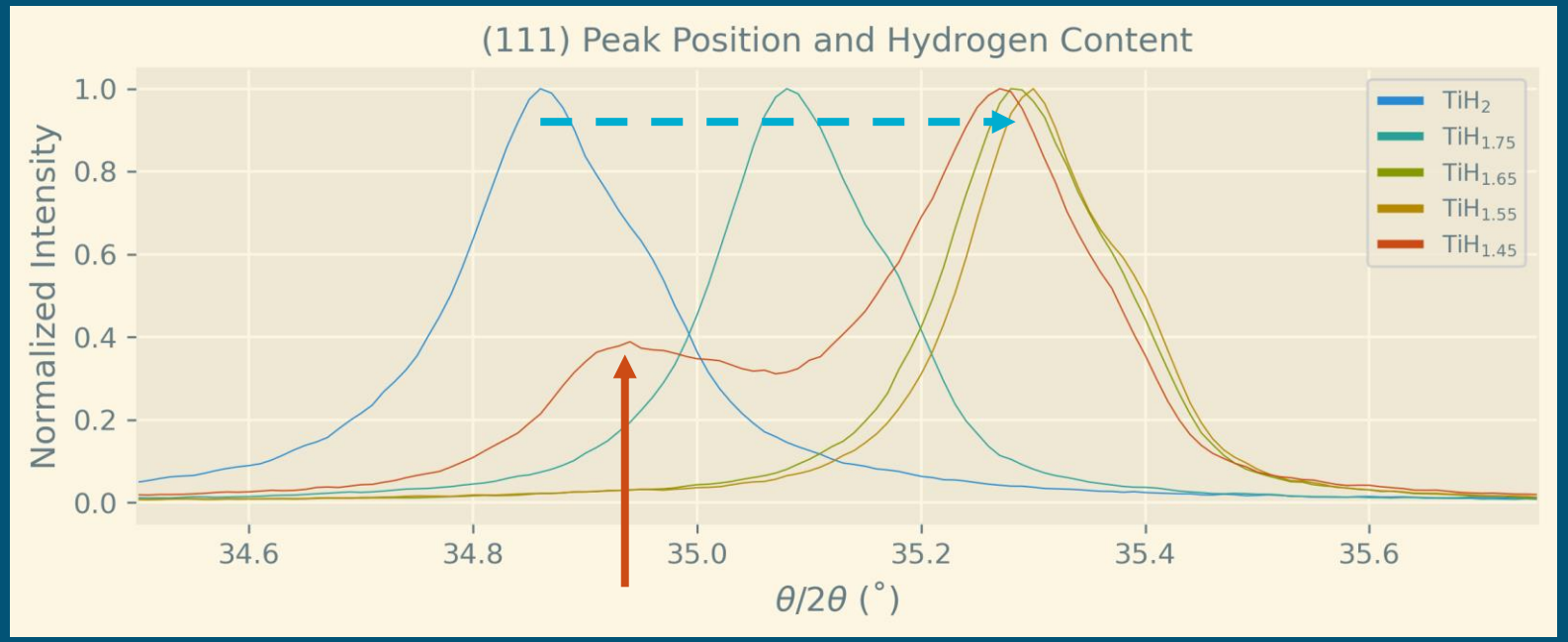
- Linear relationship between lattice parameter and TiH_x composition
  - Quantitative analysis with calibrated database
  - Corroborated using other analytical techniques (TGA, IGA, LECO)
- Phase quantitation possible via Rietveld refinement
- Current Limitations
  - Reliant on computed or measured reference
  - Signal not unique to hydrogen
  - Older data from samples with questionable purity

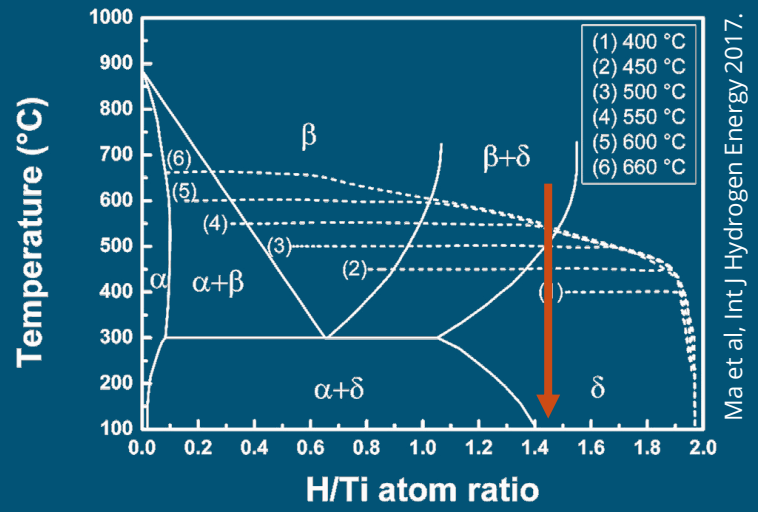


The hydrogen content of any δ-TiH_x composition can be estimated rapidly using XRD with a calibrated database

XRD application to δ-TiH_x

- XRD benefits
  - Rapid and non destructive
  - Lattice parameter proportional to hydrogen occupancy for δ-TiHx
- δ-TiH_x is stable to x ≈ 1.54
  - α-Ti begins to nucleate at room temperature when x < 1.54
  - Second phase appears as different peaks



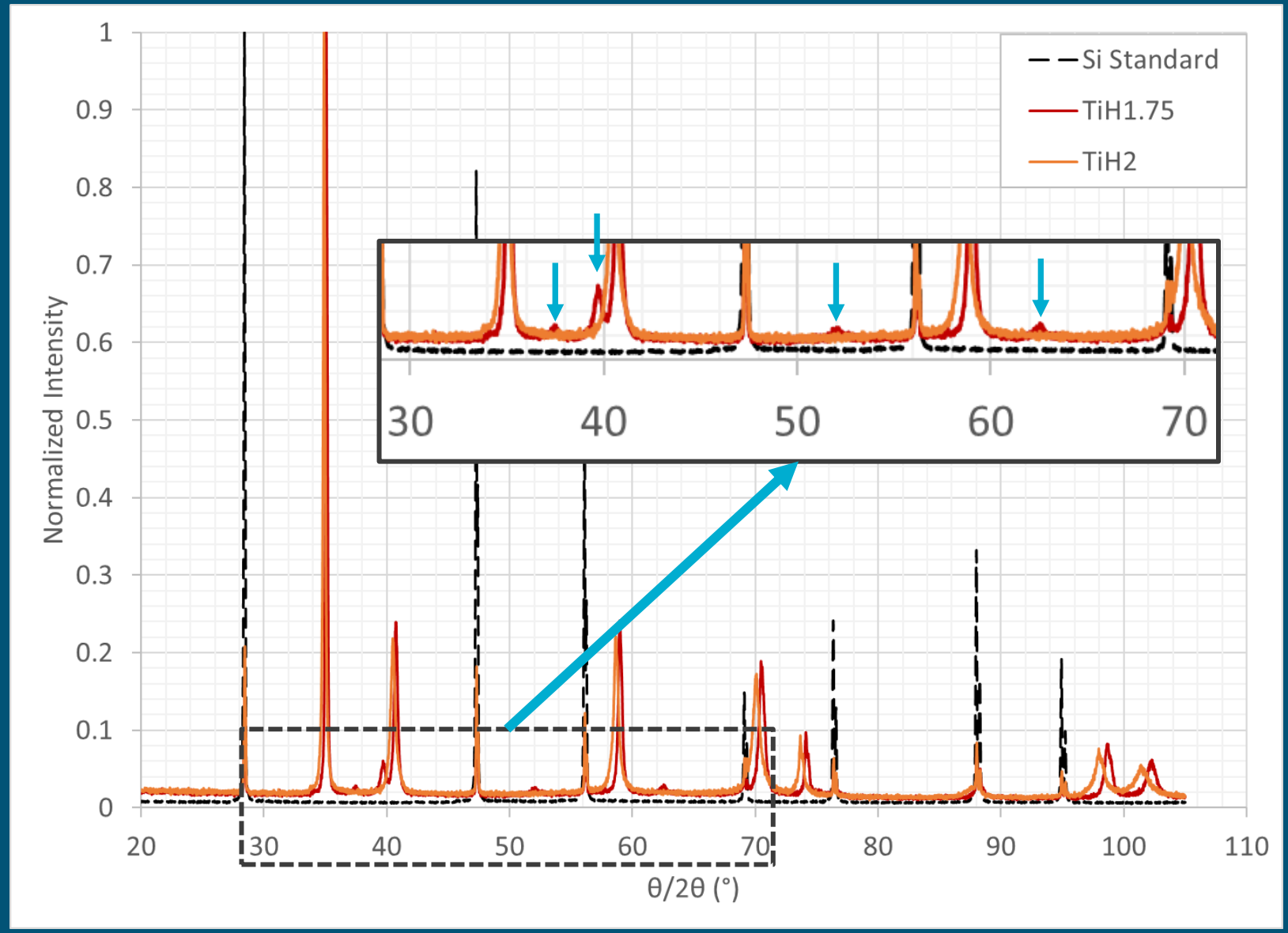


Rapid compositional analysis with phase information

XRD identification of compositional heterogeneity

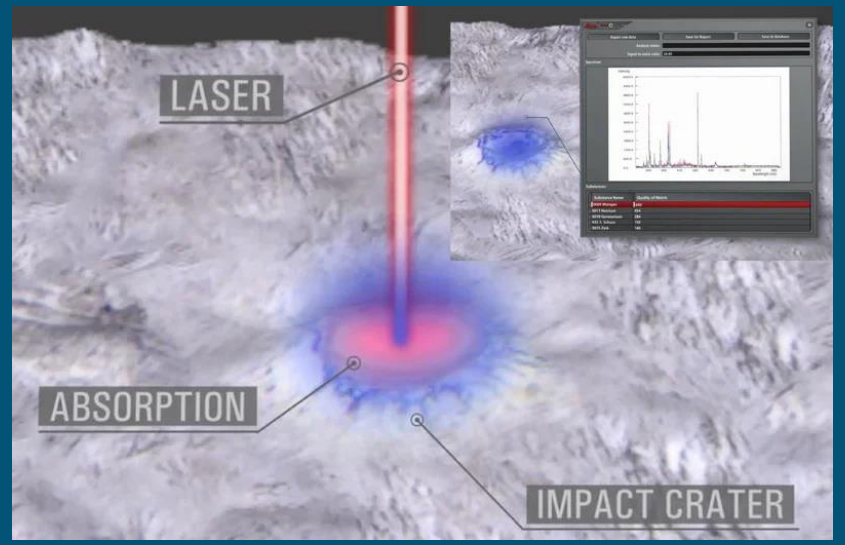
- Low intensity peaks
  - Alignment with Ti peaks
  - Doping with Si standard provides confidence in peak location
- Causal effects?
  - Equilibrium shift?
  - Contaminants/oxygen content?
  - Limitations due to solid diffusion kinetics?

Identify hydrogen distribution heterogeneity in bulk material

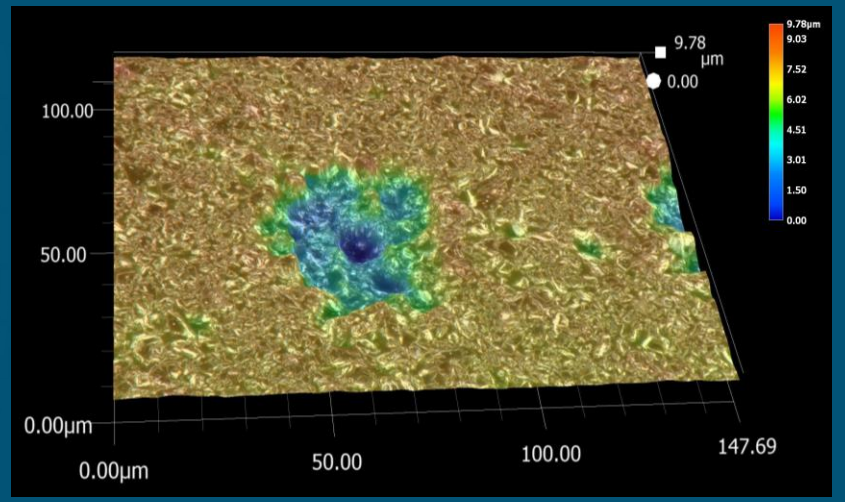


Laser-induced breakdown spectroscopy (LIBS)

- Atomic emission spectroscopy
  - Laser ablates/vaporizes a microscopic layer of the sample's surface
- Qualitative and quantitative detection of elements
  - Includes major constituents: Ti, H, O
  - Includes impurities: Mg, Na, Ca, Zn, Fe, Cr, Ni, and Zr
- Versatile sampling protocols that include a fast raster of the sample surface and depth profiling
  - Minimal sample preparation
  - Short measurement time



Keyence, Nd-YAG 355 nm



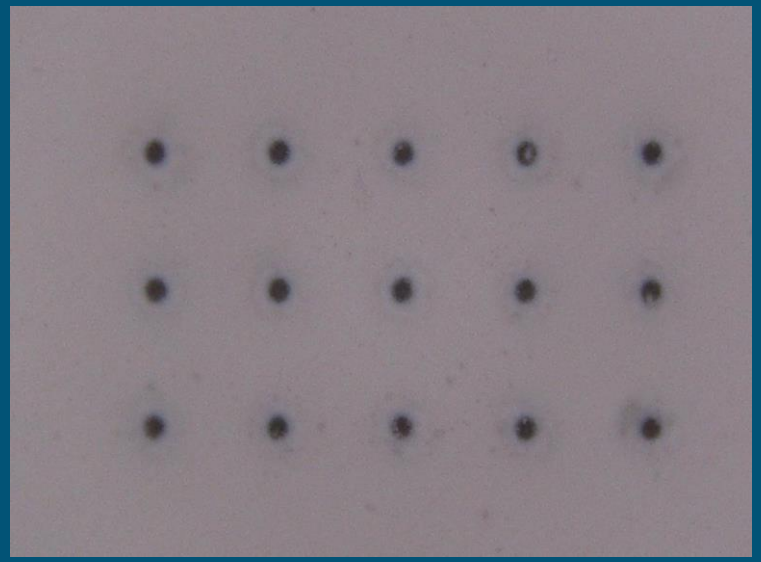
Rapid compositional analysis able to identify major constituents AND impurities

LIBS is a valuable compositional interrogation tool for δ-TiH_x

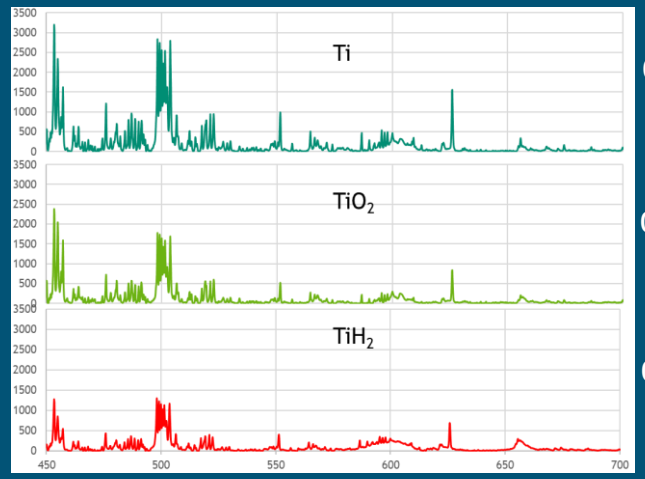
- Semi-quantitative compositional assessment
  - Proportional variation in composition
  - Assess statistical uncertainty and variation
- Current limitations of methodology
  - Sampling conducted in air
  - Commercial Ti, TiO_2, and TiH_2 materials used for spectrum reference
- Compositional identification
  - Apply linear regression to determine combination of pure material reference spectrums that represent the measured spectrum
  - Focused on major constituents: Ti, H, O

Readily assess both compositional variation and statistical uncertainty

LIBS craters in TiO_2 after sampling



No.	Presumed material	Ti	O
1	Titanium compound	30.9%	69.1%
2	Titanium compound	29.9%	70.1%
3	Titanium compound	29.7%	70.3%
4	Titanium compound	32.1%	67.9%
5	Titanium compound	30.0%	70.0%
6	Titanium compound	30.0%	70.0%
7	Titanium compound	28.6%	71.4%
8	Titanium compound	27.4%	72.6%
9	Titanium compound	27.2%	72.8%
10	Titanium compound	27.5%	72.5%
11	Titanium compound	31.7%	68.3%
12	Titanium compound	29.9%	70.1%
13	Titanium compound	29.8%	70.2%
14	Titanium compound	24.8%	75.2%
15	Titanium compound	32.6%	67.4%

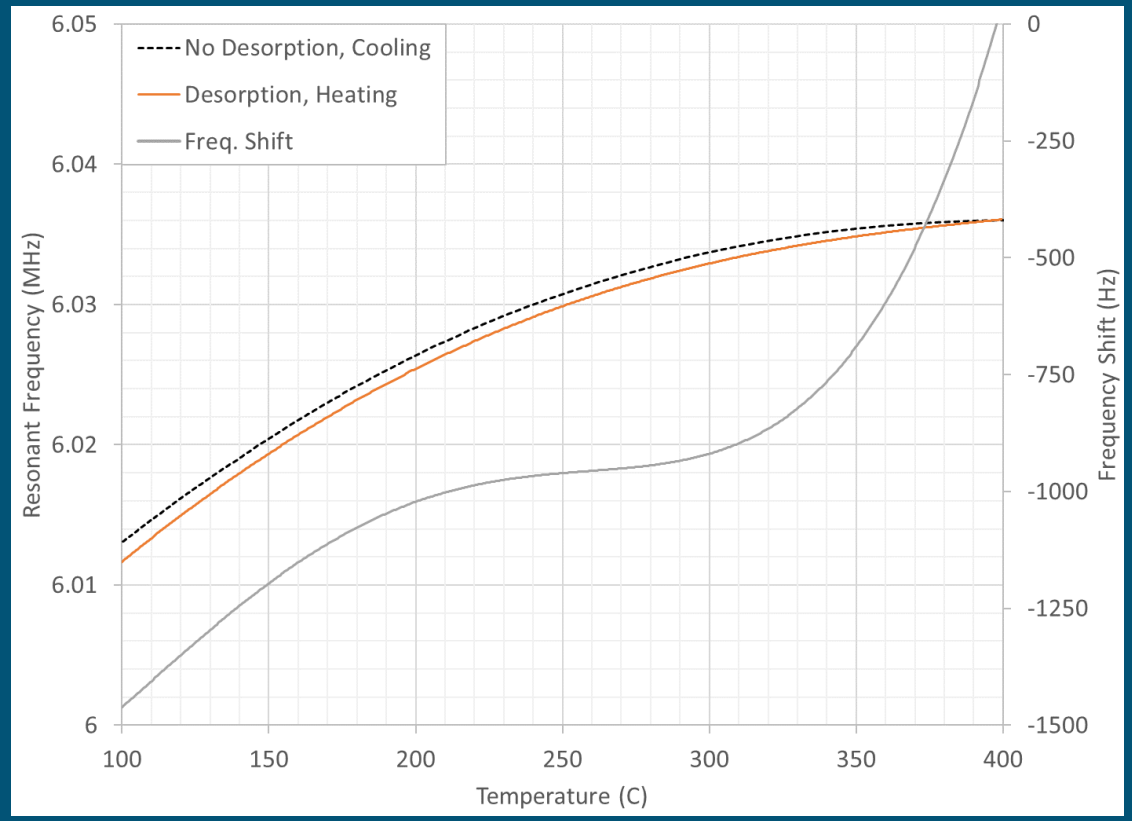


Extended interrogation via Quartz Crystal Microbalance (QCM)

- Fundamental theory – Sauerbrey Equation
  - Oscillating frequency of a piezo electric crystal is directly correlated to the mass deposited on the crystal
  - Change in frequency equivalent to mass change
  - "Tuning a drum with dampeners"

$$\Delta f = -\frac{2f_o(T)^2}{A\sqrt{\rho_q \mu_q}}\Delta m$$

Δf – Frequency Shift (Hz)
Δm – Mass Change (g)
$f_o(T)$ - Resonant Frequency (Hz)
A – Active Area (cm^2)
ρ_q - Density of Quartz (g/cm^3)
μ_q - Shear Modulus of Quartz ($g/cm*s^2$)

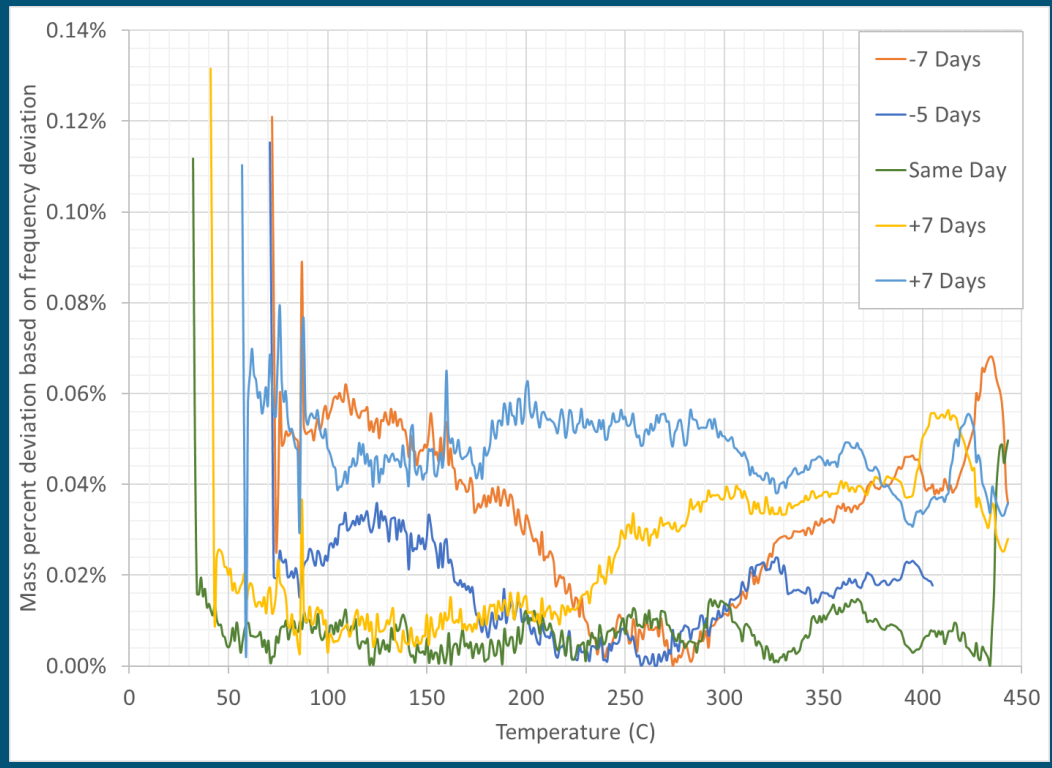


- Suited for improved environmental and process control compared to traditional TGA

Extend beyond state variation assessment and explore response between pre- and post-processed material states

Developing QCM application for δ-TiH_x characterization

- High temperature QCM system
  - Modified 6MHZ Colnatec Phoenix system
  - Up to 2mg drop cast powder samples
  - Duplication of manufacturing controls
- Current development efforts
  - Filtering out thermal-mechanical crystal response
  - Characterization of measurement variation
  - Mass quantification validation
- Replication of equilibrium processing methods:
  - Absorption and desorption behavior
  - Diffusion kinetics
  - Process path response to variations in P-T, heating rates, and reactant availability (H vs O)
  - Generate P-C-T curves (Mass quantification)



Detailed interrogation of process pathway and evolution of equilibrium states

Synergistic application of methods permits unprecedented exploration and tuning of manufacturing processes

- Rapid assessment for QA/QC
- Broadly captures phase shifts and lattice/compositional changes
- Informs on composition heterogeneity of bulk powder

- Identifies presence of impurities
- Assess compositional variation and uncertainty
- Comparing to XRD helps affirm hydrogen quantification

- Understand equilibrium evolution during processing
- Extend fundamental understanding of hydriding process
- Assess sensitivity to manufacturing process changes
- Tune manufacturing process for desired outcome

Acknowledgements: Shaun Hightower and Melody Teixeira