

# Combinatorial and High-Throughput Approaches for Thin Films: Application to Hydrogen Storage Materials

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**A DOE-EERE/NIST Joint Workshop  
November 5-7, 2008**

# Contributors:

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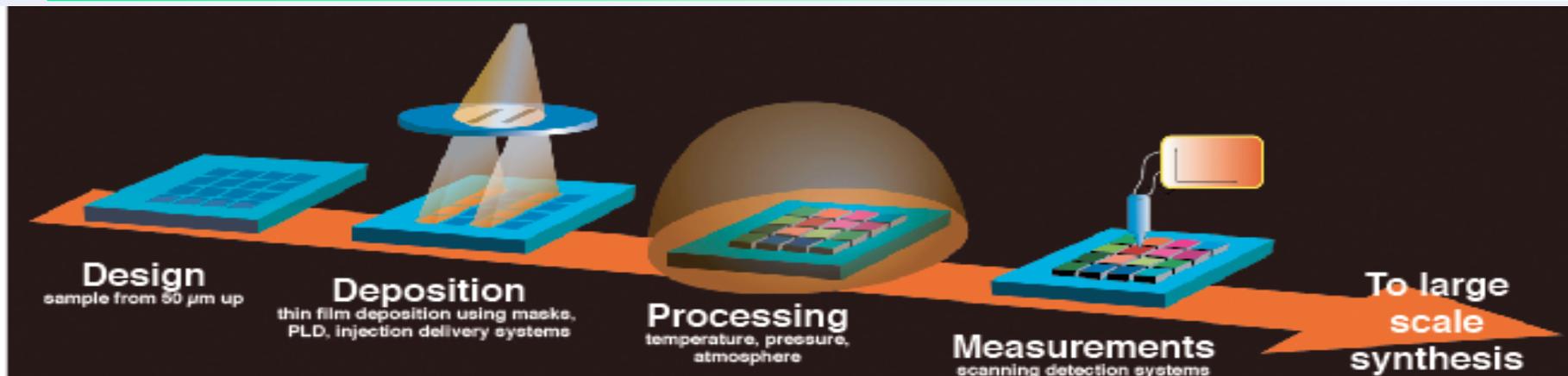
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# Combinatorial Materials Research



## Synthesis

- Array of miniature samples with different compositions, structures, surfaces, doping etc
- One-step reproducible process
- Scalable
- Characterization

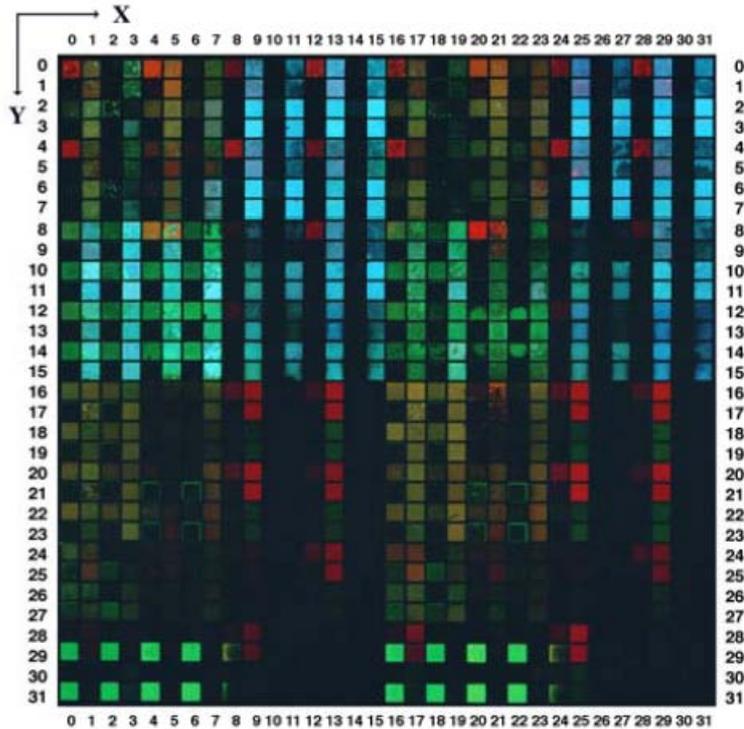
## Measurements/Property

- Methods to measuring the needed property for small-scale samples
- Parallel or high-throughput acquisition of a signal
- Correspondence between small-scale and large-scale measurements

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# Combinatorial Materials Research



Identification of an efficient blue photoluminescent composite material,  $Gd_3Ga_5O_{12}/SiO_2$ .

(from X.-D. Xiang, Peter G. Schultz et al., Science 1998)

- Multiple discrete compositions by mask-control physical vapor deposition
- Parallel acquisition of signal (images)
- Scalability

**Thin-film combi approach has been applied to many materials science problems.**

**Can the thin film approach be applied for evaluation of the materials for hydrogen storage?**

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# Evaluation of Hydrogen Storage Materials (HSM)

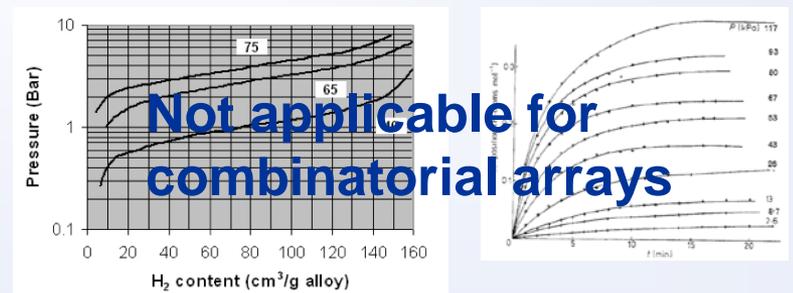
Table 1. DOE Technical Targets: On-Board Hydrogen Storage Systems<sup>a, b, c</sup>

Storage Parameter	Units	2007*	2010	2015
Usable, specific-energy from H <sub>2</sub> (net useful energy/max system mass) <sup>d</sup> ("Gravimetric Capacity")	kWh/kg (wt.% hydrogen)	1.5 (4.5%)	2 (6%)	3 (9%)
Usable energy density from H <sub>2</sub> (net useful energy/max system volume) ("Volumetric Capacity")	kWh/L (kg H <sub>2</sub> /L)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost <sup>e</sup>	\$/kWh net (\$/kg H <sub>2</sub> )	6 (200)	4 (133)	2 (67)
Fuel cost <sup>f</sup>	\$ per gallon gasoline equivalent at pump	3	1.5*	1.5*
Operating ambient temperature <sup>g</sup>	°C	-20/50 (sun)	-30/50 (sun)	-40/60 (sun)
Cycle life (1/4 tank to full) <sup>h</sup>	Cycles	500	1000	1500
Cycle life variation <sup>i</sup>	% of mean (min) @ % confidence	N/A	90/90	99/90
Minimum and Maximum delivery temperature of H <sub>2</sub> from tank	°C	-20/85	-30/85	-40/85
Minimum full-flow rate	(g/s)/kW	0.02	0.02	0.02
Minimum delivery pressure of H <sub>2</sub> from tank; FC=fuel cell, I=ICE	Atm (abs)	8 FC 10 ICE	4 FC 35 ICE	3 FC 35 ICE
Maximum delivery pressure of H <sub>2</sub> from tank <sup>j</sup>	Atm (abs)	100	100	100
Transient response 10%-90% and %-0% <sup>k</sup>	s	1.75	0.75	0.5
Start time to full-flow at 20°C <sup>l</sup>	s	4	4	0.5
Start time to full-flow at minimum ambient <sup>l</sup>	s	8	8	2
System Fill Time for 5-kg hydrogen	min	10	3	2.5
Loss of useable hydrogen <sup>m</sup>	(g/h)/kg H <sub>2</sub> stored	1	0.1	0.05
Permeation and leakage <sup>n</sup>	Sc/h	Federal enclosed-area safety-standard		
Toxicity		Meets or exceeds applicable standards		
Safety		Meets or exceeds applicable standards		
Purity <sup>o</sup> (H <sub>2</sub> from storage system)		98% (dry basis)		

- Density of hydrogen in HSM
- Temperature and Pressure of absorption/desorption cycle
- Kinetics of the cycle

## Typical evaluation of bulk HSM:

- Volumetric PCI (Sievert)
- Thermogravimetric analysis (TGA)
- Electrochemical charging

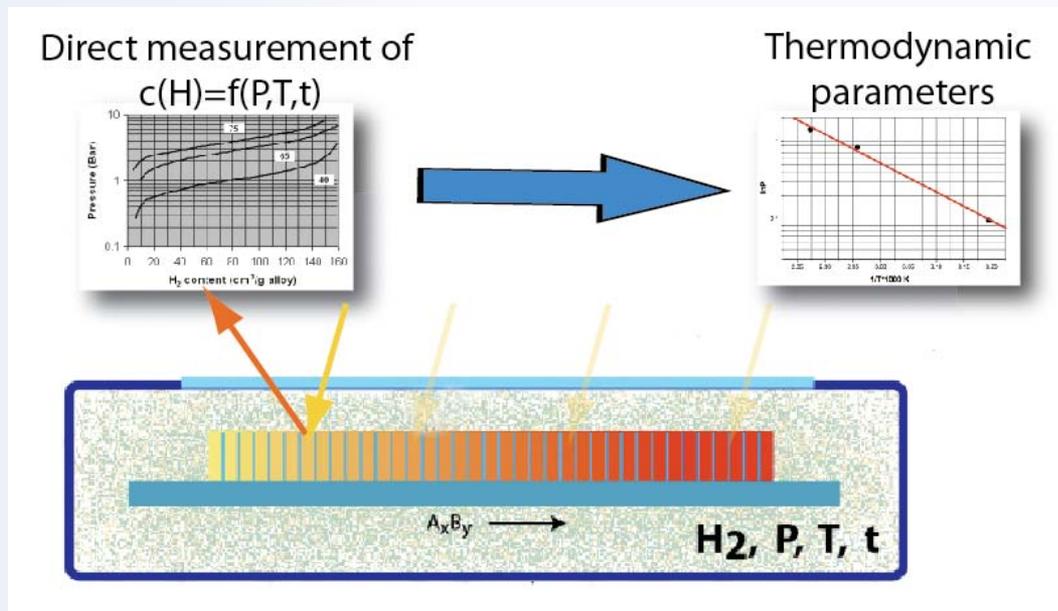


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# Combinatorial Approach for Hydrogen Storage Materials

## Ideal direct measurements



### Local measurements of hydrogen content $c(H)$ :

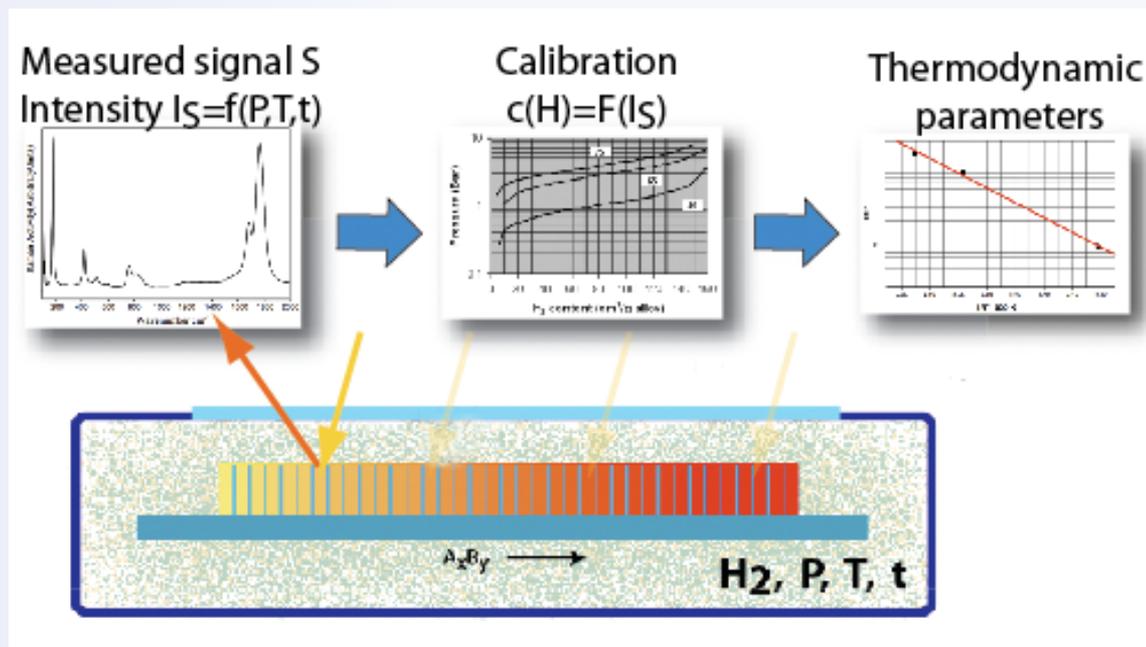
- Spectroscopic Prompt Gamma Activation Analysis (PGAA) - neutron beam-based "EDS" for hydrogen. Available at NCNR;
- Electrochemical ?

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# Combinatorial Approach for Hydrogen Storage Materials

## In-direct measurements



### Different research groups:

- Optical
- IR
- Resistivity
- Nanocalorimetry
- Stress
- XRD

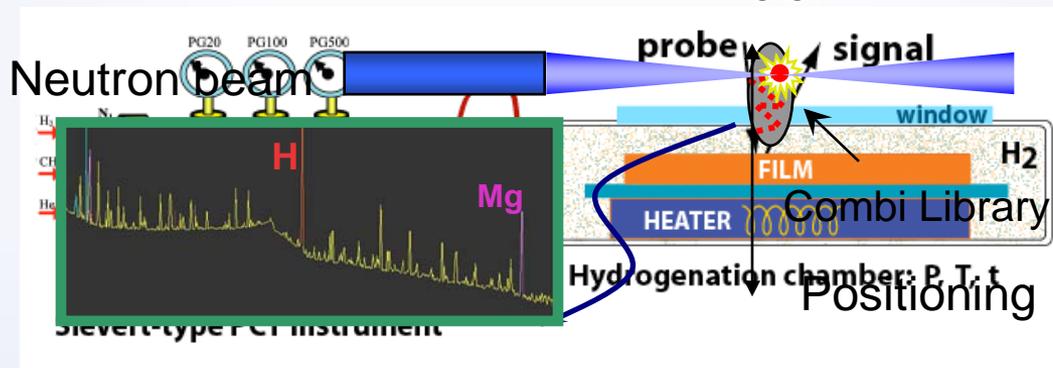
### NIST program:

- IR emissivity
- FTIR
- Raman

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# NIST Approach to Combinatorial Hydrogen Storage Materials Studies

- Developing different **in-direct measurement** of good spatial resolution, such as IR emissivity, FTIR or Raman, to monitor **in-situ** hydrogenation of combinatorial samples (thin films).
- Developing instrument for **simultaneous volumetric and in-direct measurements** of small samples (e.g., thin films) for calibration purposes.
- Use **Prompt Gamma Activation Analysis (PGAA)** to calibrate (and understand) our in-direct measurements.
- With advances in intensity and optics of the NIST reactor neutron beam lines, to do **direct in-situ combinatorial measurements** using gradient films.



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# NIST Approach: In-direct measurements

## IR emissivity measurements

Measuring optically the increase of electrical resistivity due to the presence of hydrogen (Hagen-Rubens relation) - good for metal-insulator transitions

- Effect of composition and microstructure (e.g., Mg-TM films) - combi
- Effect of catalytic coating (thickness, composition) - combi
- Correlation of IR intensity with PGAA measurements - SC films

## Raman and FTIR spectroscopy

Measuring evolution of vibration spectra, structural characteristics - good for complex hydrides

- In-situ hydrogenation of powders (complex hydrides) and films - SC
- Set-ups for parallel Raman/FTIR spectra acquisition and volumetric Sievert measurements; calibration of a signal and intensities - SC
- Scanning Raman/FTIR on combinatorial arrays/films - combi

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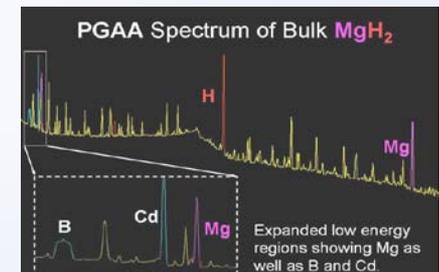
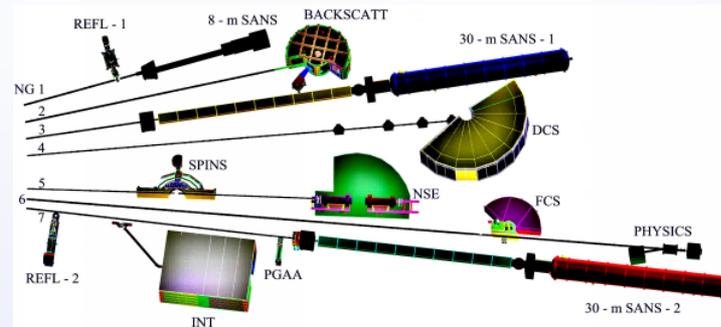
# Prompt Gamma Activation Analysis (PGAA)

## Principles of PGAA

1. Sample is irradiated in a beam of neutrons. Nuclei of most elements undergo neutron capture, emit prompt gamma-rays upon de-excitation of nuclei
2. Measurement of gamma-rays by high resolution germanium detector yields qualitative and quantitative analysis.
3. Use of “cold” neutrons enhances sensitivity.

## Advantages of PGAA

1. Multielement, nondestructive analysis.
2. Bulk analyses (neutrons and gamma rays penetrate sample).
3. Independent of element’s chemical form. Especially useful for low Z elements (e.g. H, B, C, N, S, Cl)
4. Hydrogen peak at 2223 keV has few interferences
5. Focused or collimated neutron beam may be used for compositional mapping of samples.



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# Making the PGAA Combi

## Three Analytical Challenges

### Analysis of thin film specimens

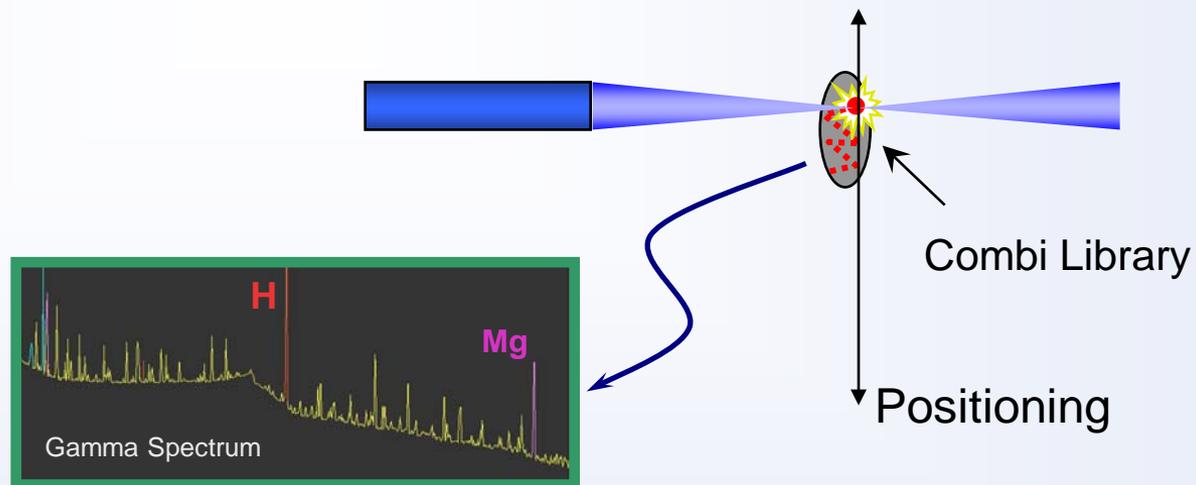
- Library Arrays (0.3-5  $\mu\text{m}$ ) thick film
- PGAA of Mg and Y film
- Compositional spread film Mg-Ti

### In-situ hydrogenation

- Temperature, Pressure
- $\text{H}_2$  gas background
- Absolute Positioning
- Time of acquisition
- Safety issues, hydrogen embrittlement

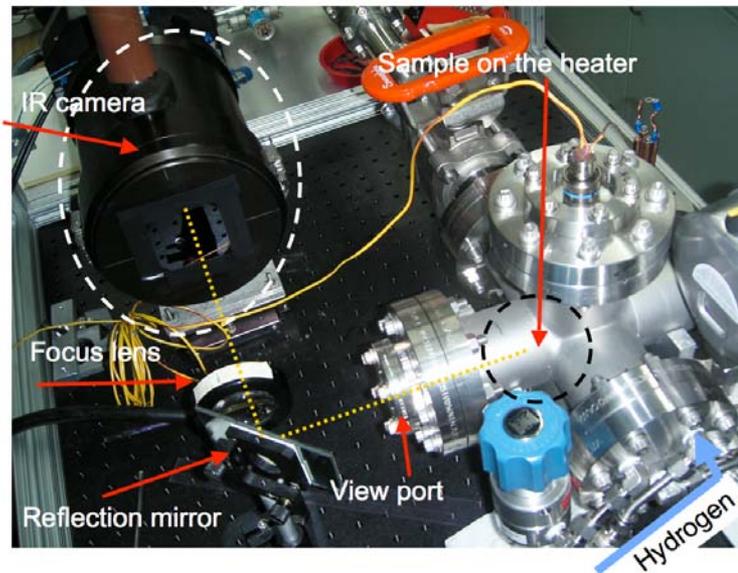
### Spatial Mapping

- Neutron Optics
- Gain in Quantitation
- Gain in Resolution

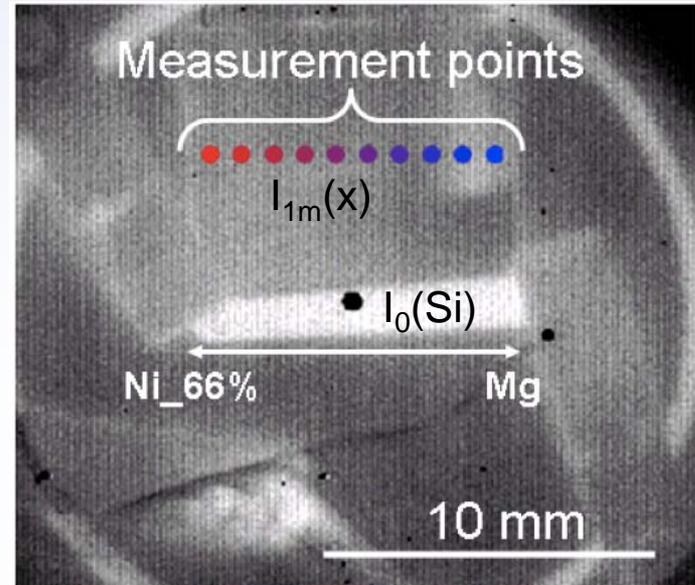


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# IR emissivity imaging of in-situ hydrogenation of films



A hydrogenation chamber (0-10 bar) with a heating stage (RT-500 °C).  
 IR emission images are continuously collected every 30 sec through a sapphire window.  
 The IR camera: 256x256 array of InSb diodes permits “snap-shot” imaging (10 microsecond).  
 The camera: peak sensitivity at 5  $\mu\text{m}$ , integrated range of 1.0 to 5.5  $\mu\text{m}$ .

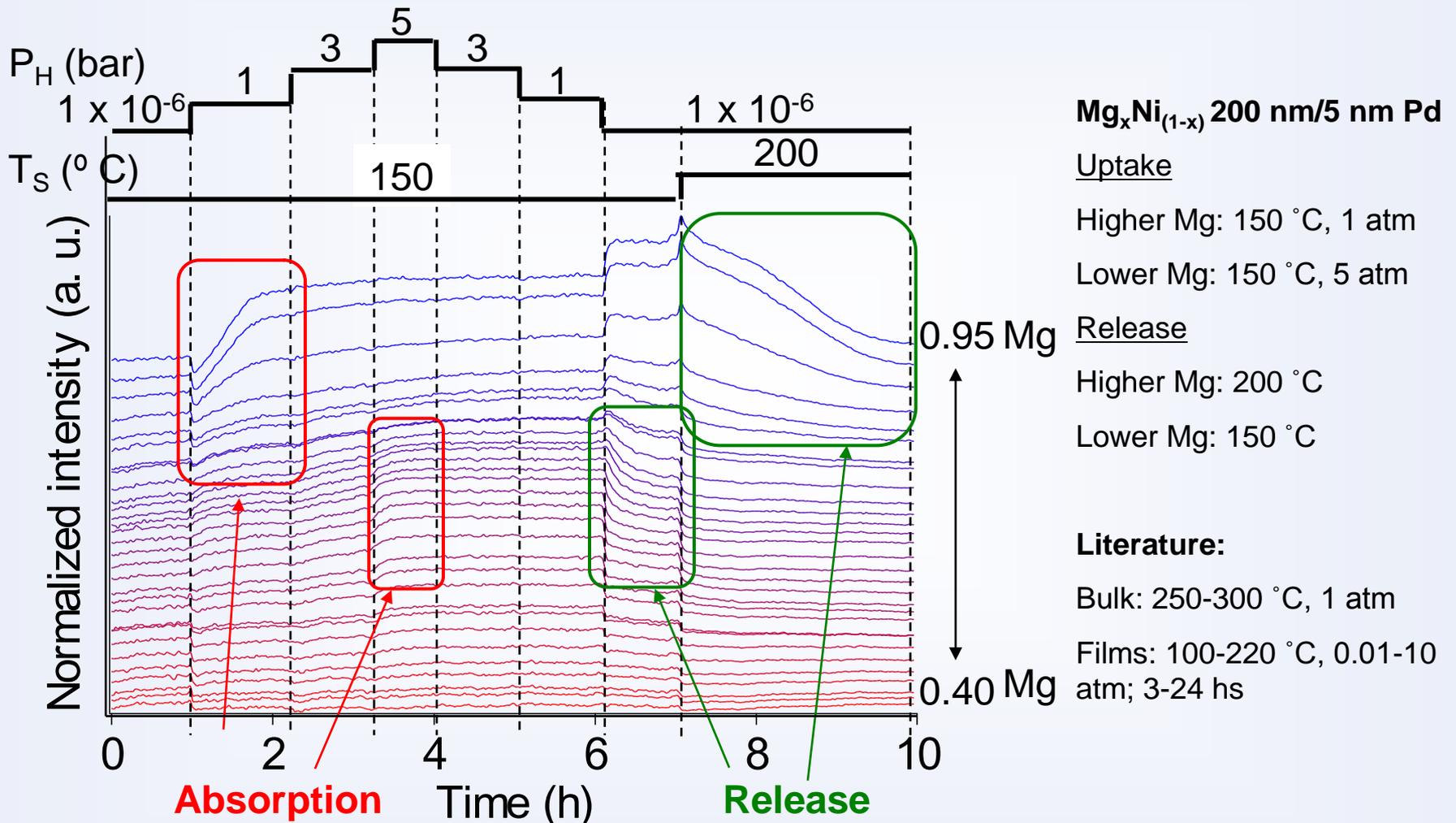


For each frame a normalized intensity of selected points (corresponding to composition  $x$ ) is calculated:  $I_{mxN} = I_{mx} / I_{0m}$ . ( $I_{0m}$  is from an  $\text{SiO}_2$  exposed substrate).

The normalized intensities  $I_{mxN}$  are plotted as a function of frame number (time, pressure or temperature)

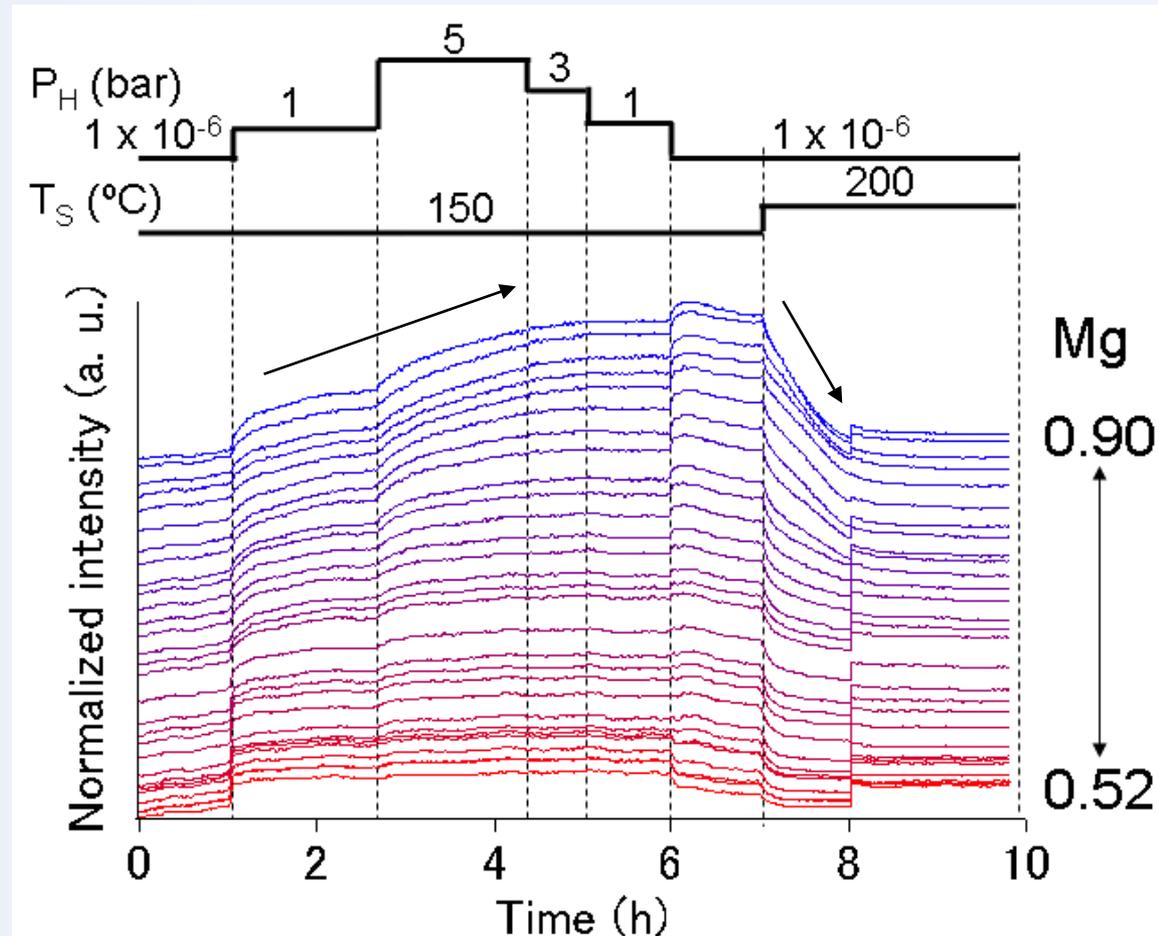
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# IR imaging of hydrogenation of $Mg_xNi_{(1-x)}$ thin film



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# IR imaging of hydrogenation of $Mg_xTi_{(1-x)}$ thin film



$Mg_xTi_{(1-x)}$  200 nm/5 nm Pd

Uptake

150 °C, 1-5 atm

Release

200 °C

**Literature:**

Films: RT, 1 atm; 100 s

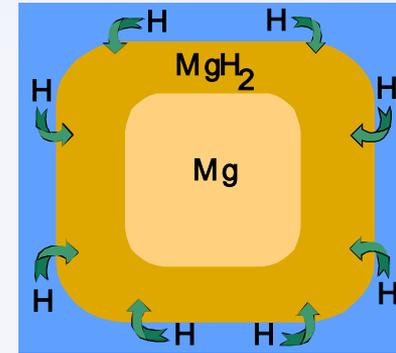
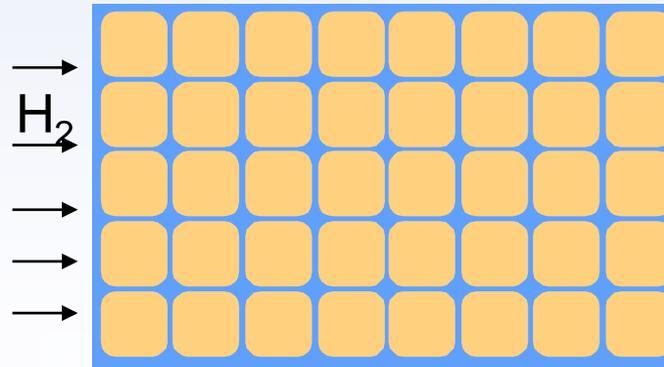
Kinetics improved with Ti

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# Combinatorial Mg-(Transition Metals) films

- High capacity of  $MgH_2$
- Slow kinetics, high temperatures for bulk
- Improvement for nanoscale microstructure



hydride-forming phase
  high H diffusivity phase

## Microstructural design:

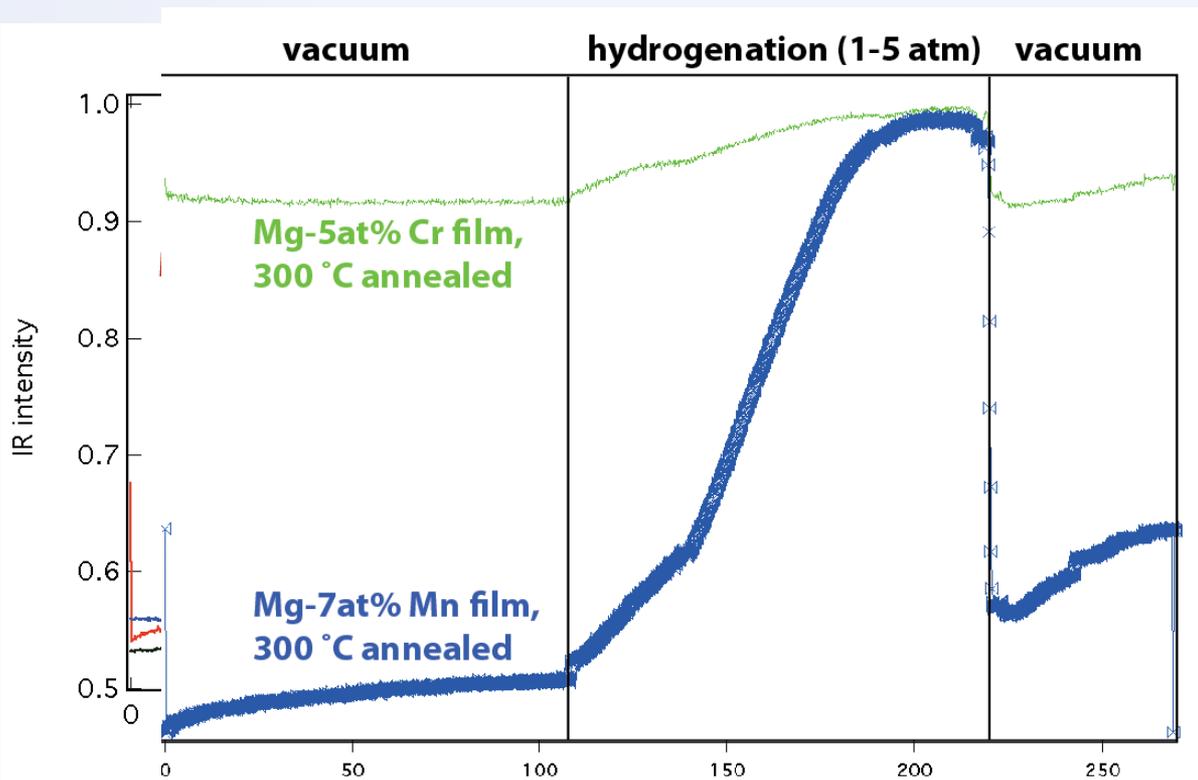
Two-component systems where one component is a hydride-forming phase, and another - a phase with high diffusivity of hydrogen without forming a hydride phase

Use immiscibility of Mg-TM systems

Sc 1 comp.  -8	Ti no comp.  +20	V no comp.  +31	Cr no comp.  +32	Mn no comp.  +12	Fe no comp.  +23	Co 1 comp.  +1	Ni 2 comp.  -8
Y 3 comp.  -12	Zr no comp.  +5	Nb no comp.  +44	Mo no comp.  +50	Tc no info.  +1	Ru 2 comp.  -3	Rh 3 comp.  -28	Pd 6 comp.  -63
La 5 comp.  -13	Hf no comp.  +11	Ta no info.  +41	W no comp.  +53	Re no info.  +28	Os comp. exist  +5	Ir 2~3 comp.  -22	Pt 5 comp.  -55

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# Combinatorial Mg-(Transition Metals) films



Effect of microstructure (annealing) on hydrogenation response  
Effect of TM on hydrogenation response

TM: Cr, Mn, Mo, Nb,  
Ru, Ti, Zr, Hf

Discreet compositions,  
from 1 to 8 at% TM

Films capped with Pd

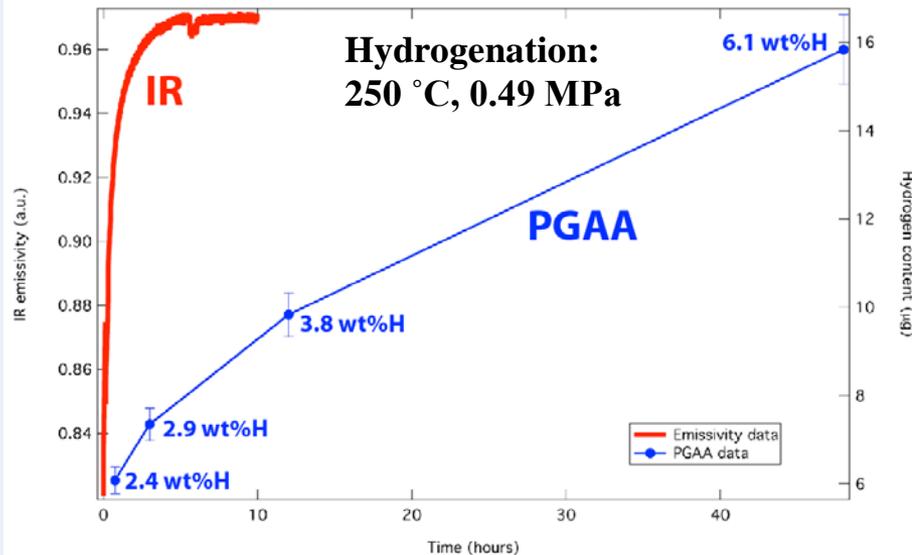
Hydrogenation  
conditions:

150 °C, hydrogen  
pressure from 1 to 5  
atm

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# IR emissivity, PGAA and FTIR of Mg films

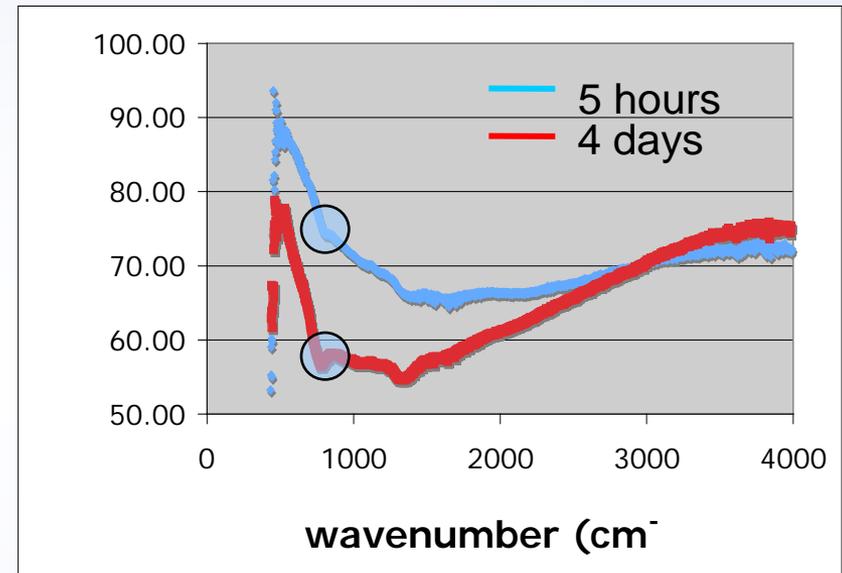
## Comparing IR emissivity and PGAA



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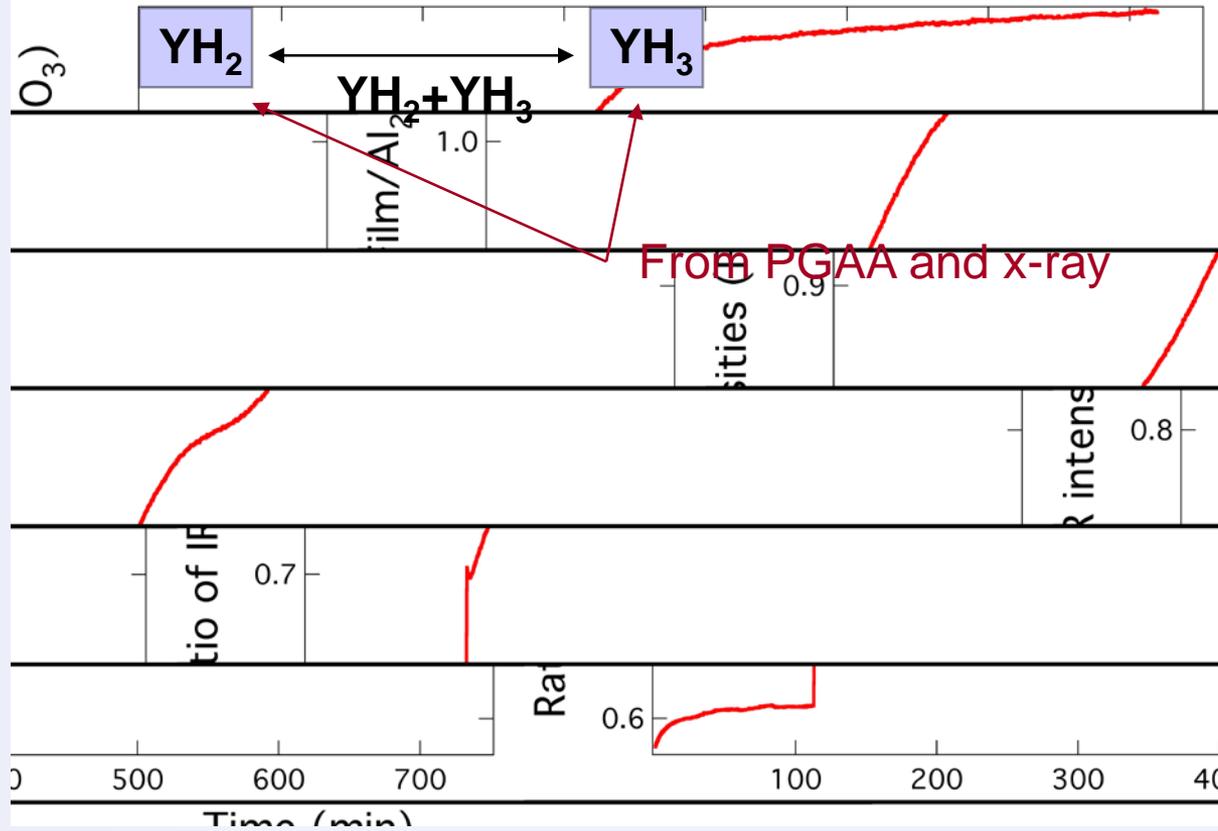
## Evolution of FTIR spectra



Change in the  $\text{MgH}_2 \text{A}_{2u}$  band intensity is ~34%. This is comparable to the change in hydrogen content seen with PGAA

# IR emissivity of hydrogenated Y film

Hydrogenation at 150 °C, 5 atm H<sub>2</sub>, Pd-coated Y film



YH<sub>2</sub> - cubic CaF<sub>2</sub>-type, metallic

YH<sub>3</sub> - hexagonal, insulator (transparent)

IR emissivity captured both metal-metal (Y-YH<sub>2</sub>) and metal-insulator (YH<sub>2</sub> - YH<sub>3</sub>) transitions

From Kremers et al., PRB, 57 (1998)

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# Summary

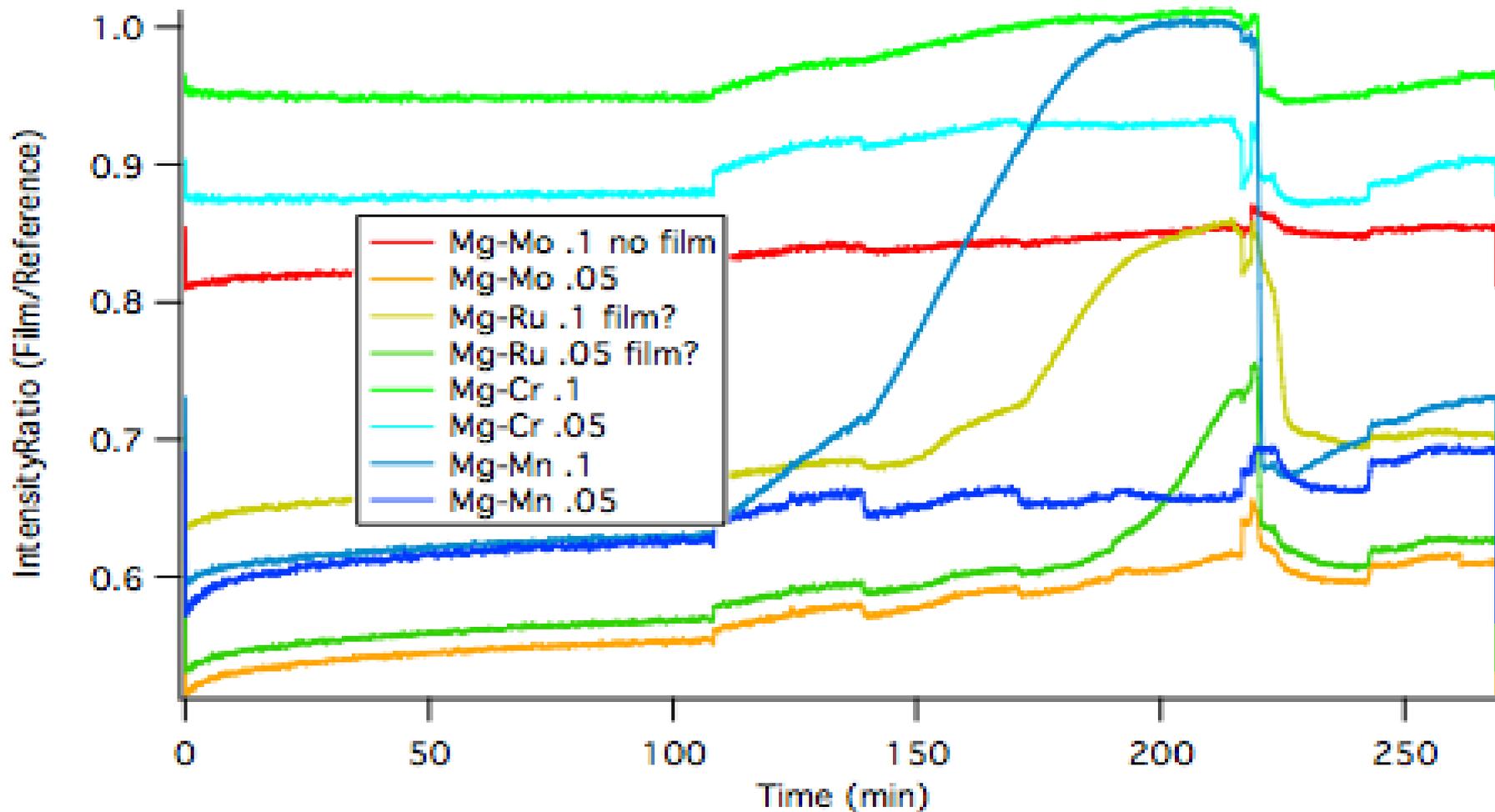
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- MSEL/NIST hydrogen storage program - developing combinatorial methods for evaluating hydrogen storage materials using both direct and in-direct measurements
- In-situ IR emissivity imaging is used as a screening tool for hydrogenation reactions, e.g. for Mg-TM films
- In-situ Raman and FTIR spectroscopy, along with calibrations, can provide both screening, evaluation and structural information of hydrogenation
- PGAA shows promises as a tool for direct combinatorial measurements, as well as a calibration technique for our combinatorial in-direct measurements.

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# Combinatorial Mg-(Transition Metals) films



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# Relationship between IR emissivity and hydrogenation

- Kirchhoff's law of thermal radiation ( $\varepsilon$  - emissivity,  $R$  - reflectivity)

$$1 - \varepsilon = R$$

- Hagen-Rubens relation (classical electron theory, holds for IR  $\lambda$ 's)

$$R(\omega) \approx 1 - \sqrt{2\omega\rho/\pi}$$

- Hydrogenation lead to changes of electronic structure, usually from metallic to insulating state, and increased electron scattering, thus the increase in resistivity and IR intensity is expected

## Other factors that may contribute to IR intensity:

- Changes of film surface roughness  $r$  (usually not for  $r \ll \lambda$ )
- Changes in temperature (enthalpy)
- Other phase transformations (e.g., surface reaction, Pd diffusion)

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