X-ray Diffraction for Characterization of Materials for Energy

Scientific Basis for Solar Energy and Energy Storage

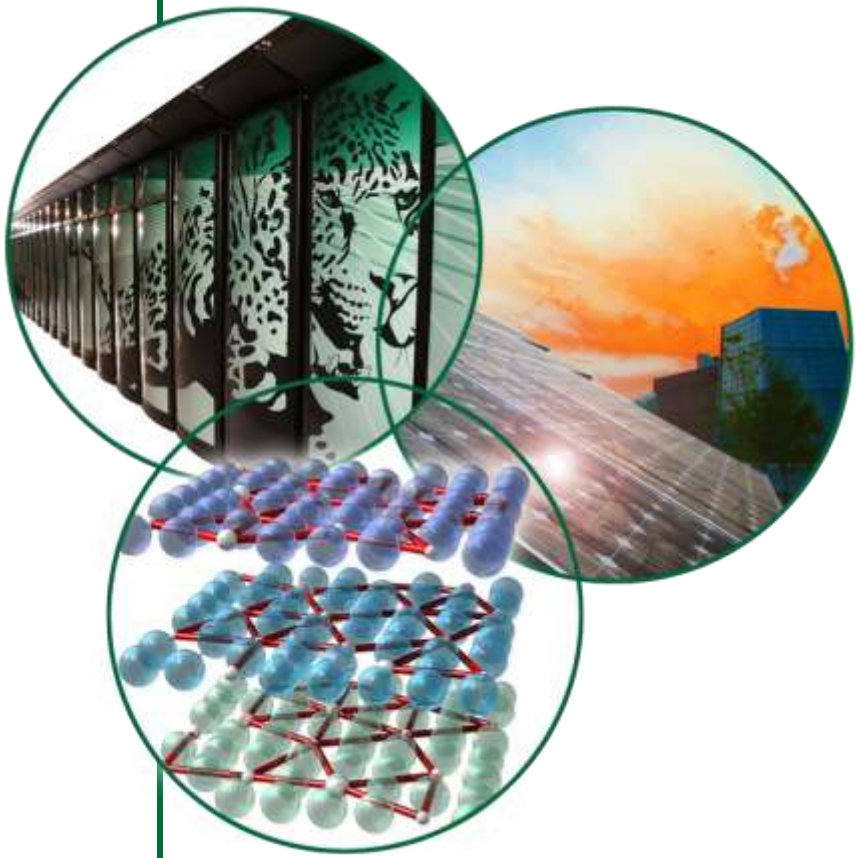
13 September 2010

Andrew Payzant

High Temperature Materials Laboratory &

Center for Nanophase Materials Sciences

Oak Ridge National Laboratory



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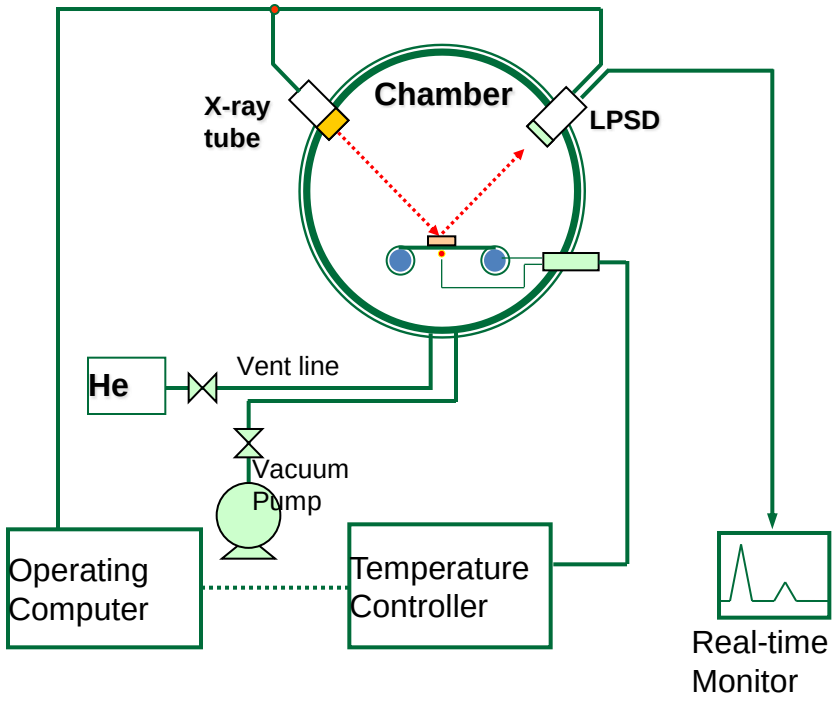
Why bother with x-ray diffraction?

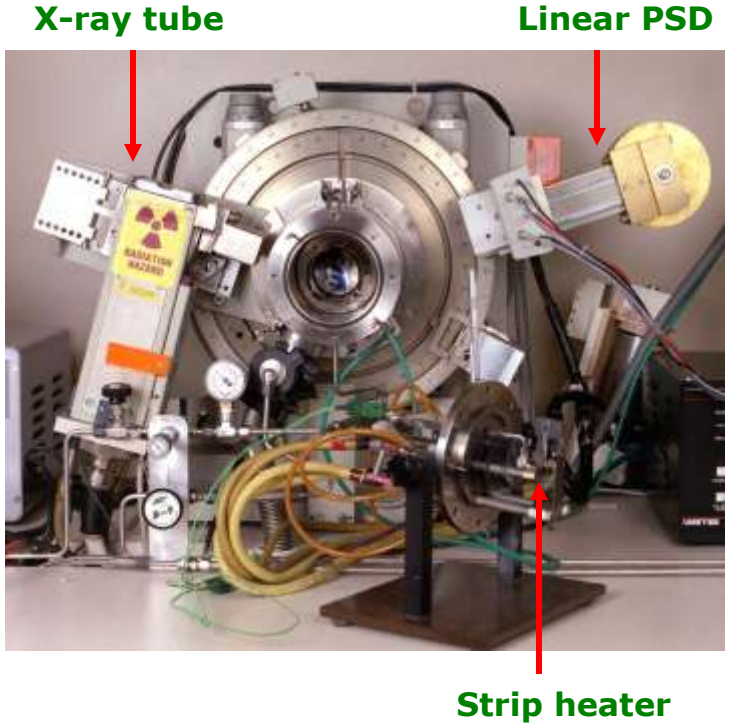
- X-ray diffraction is a very old technique. Surely it has been superceded by electron microscopy, atom probe, and other newer experimental tools? … not so!
- X-ray diffraction probes a large volume of material – much larger than TEM or atom probe
- So x-rays tell us a lot about the forest, whereas these other techniques provide exceptional detail on selected trees. Both sets of information can be very important!
- Why laboratory XRD?
  - Cost (much cheaper than synchrotron or neutron sources)
  - Accessibility

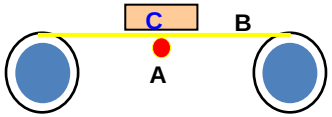
Lower instrument cost allows for dedicated specialized instruments

- **HTML XRD instruments**
  - 2-axis XRD (Cu k-alpha, PSD, multiple sample changer) *phase ID, structure refinement*
  - 2-axis MPXRD (Cu k-alpha, PSD, XRK900, HT16, MPSS, parallel-beam) *multipurpose*
  - 2-axis HTXRD (Cu k-alpha, PSD, HDK2.3, gas handling) *phase transformations*
  - 2-axis XRD (Mo k-alpha, capillary) *transmission, PDF*
  - 4-axis XRD (rotating anode Cu k-alpha, parallel-beam) *texture, stress*
  - 4-axis XRD (Co k-alpha) *texture, stress*
  - XRD stress goniometer *residual stress*
- **CNMS instruments**
  - 2-axis MPXRD (Cu k-alpha, XRK900, PSD, parallel-beam, cryostat) *multipurpose*
  - 4-axis XRD (Cu k-alpha, high-resolution, DHS900) *reflectometry, RSM, rocking curve, etc*.
  - Micro-XRF (Rh white-beam source, Si(Li) detector) *fast elemental analysis*
  - SAXS (Cu k-alpha, various stages)

Bühler HDK2.3 XRD Furnace





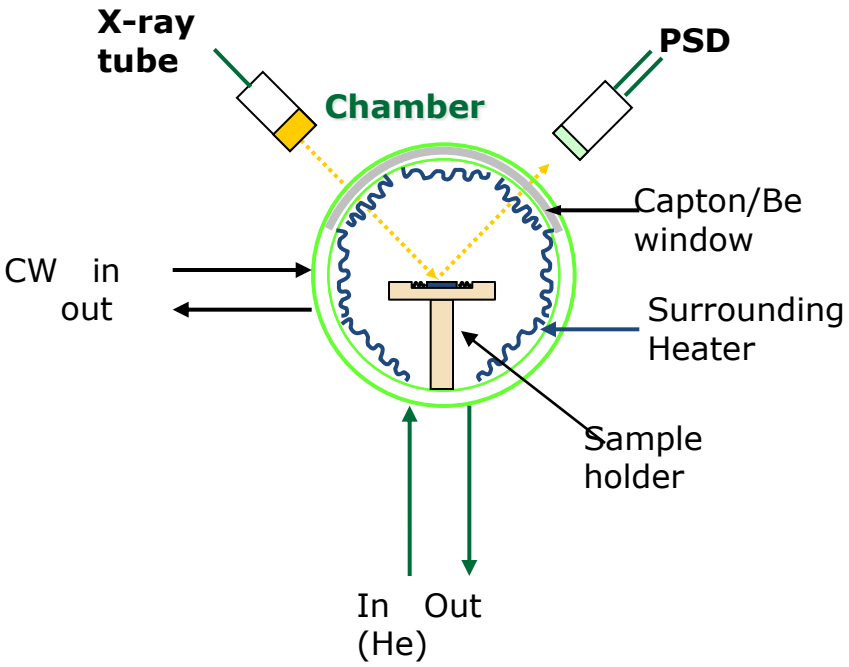


A: Spot-welded thermocouple
B: Heater strip (Pt20%Rh)
C: Sample

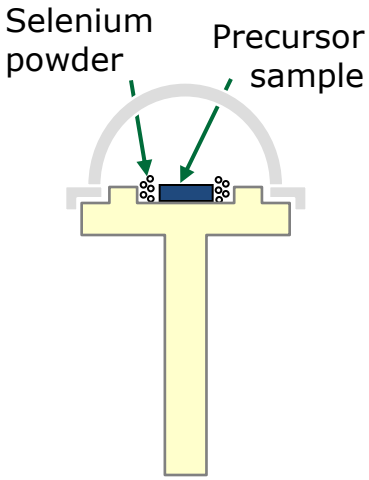
➔ **High Temperature Materials Laboratory**

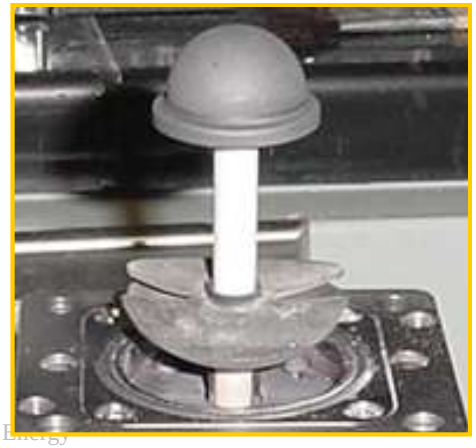
Anton Paar XRK900 Reaction Chamber

PANalytical X'Pert Pro MPD



Graphite Dome





➔**High Temperature Materials Laboratory**
➔**Center for Nanophase Materials Sciences**

Contents

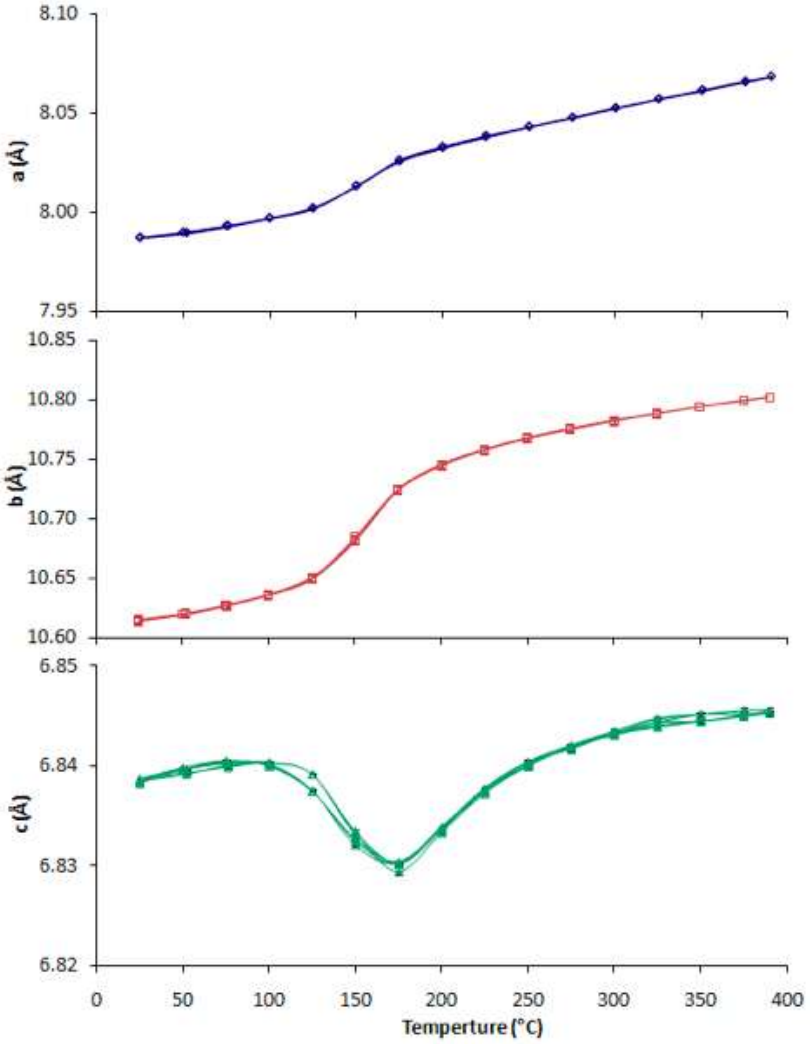
- This presentation will highlight XRD-based studies of energy-related materials including:
  - Thermoelectrics (TAGS)
  - Photovoltaics (CIGS)
  - Energy storage (Li-ion battery materials)
  - Gas separations (Pd-alloy membranes)
  - High-temperature dielectrics (Hafnium oxide)
  - Solid Oxide Fuel Cells (YSZ)

Thermoelectric materials

- There is need for thermoelectric materials that can operate at high temperature.
- In-situ HTXRD allows an investigation of the lattice parameter changes, atom site position changes, and phase stability over the temperature range of interest

In-situ XRD study of Cu_3SbSe_3 thermoelectric

- Lattice parameters of orthorhombic Cu_3SbSe_3 as a function of temperature, from high-temperature Xray diffraction
- three cycles of heating and cooling to 390°C are shown, indicating good phase stability over this range.
- The lattice parameters exhibit complex, non-linear thermal expansion, including negative thermal expansion in the *c* axis between ~100° and 175°C. How does this impact ZT?



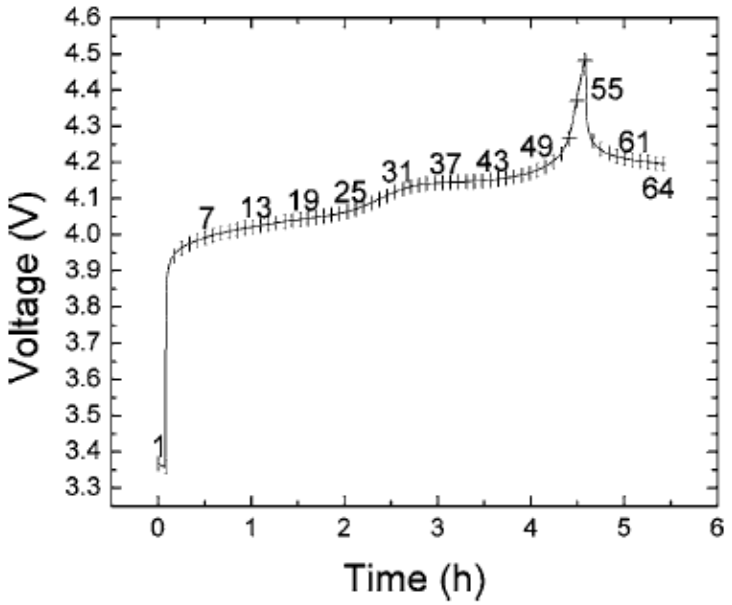
- Melanie Kirkham and Paul Majsztrik (unpublished)

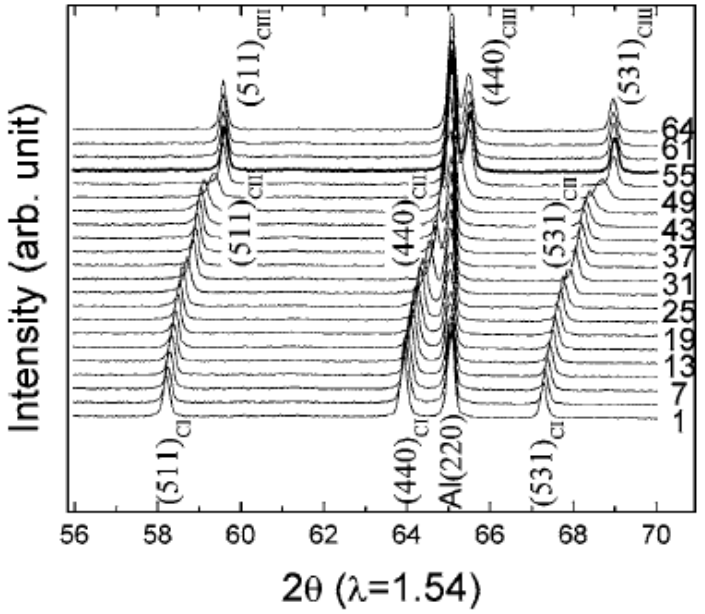
Li-ion battery materials

- Lithium (Z=3) is a weak x-ray scatterer, but the lattice dilation from lithium intercalation yields easily measured Bragg peak shifts and phase transformations that can be used to quantify the Lithium content in crystalline phases
- Cathode materials: Lithium iron phosphate $Li_{1-x}FePO_4$; "NMC" $Li_{1-x}(Ni,Mn,Co)O_2$;
- Anode materials: $Li_{1-x}C_6$; $Li4\text{-}xTi_5O_{12}$; $Li_{5-x}Si$; etc
- Requires x-ray transparent windows (e.g., aluminized mylar, kapton, beryllium, etc.)
- Both laboratory and synchrotron x-ray sources used.

CRADA: A123 Systems, Dow Kokam, LLC, Planar Energy Devices
HTML User Program: Valence Technologies, U Mich, BNL, NREL, UTK/ORNL, GM

In-situ XRD study of Li-ion battery

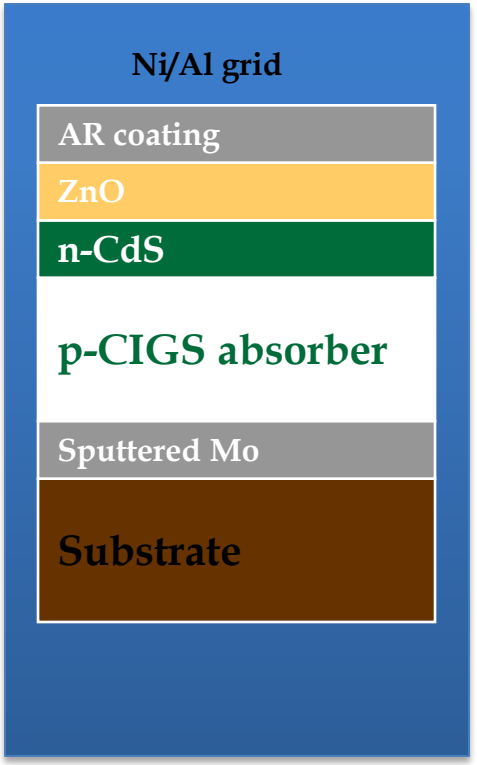




- Charge curve and in-situ XRD patterns of $LiMn_2O_4$ during first charge to 4.5 V at room temperature
- Ref: Chung *et al., J. Electrochem. Soc., 153, A774-A780 (2006)*
- ***Experiments done at the National Synchrotron Light Source, X14A***

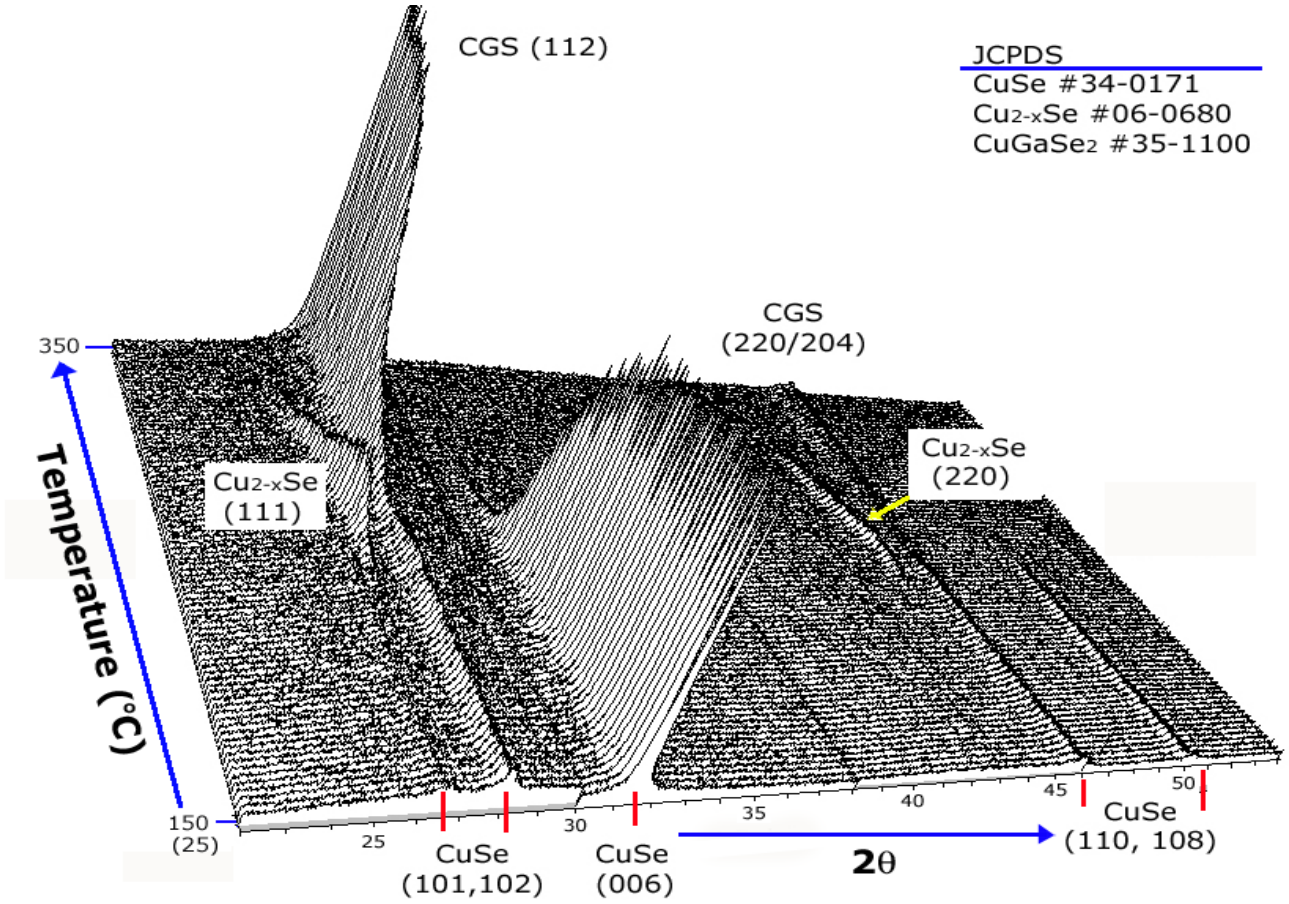
Thin-film photovoltaic materials

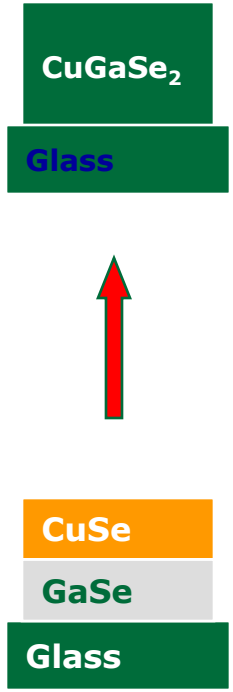
- CIGS ($CuIn_xGa_{1-x}Se_2$) solar cells have measured efficiencies as high as 19.3% (NREL report, 2005)
- These are direct-gap semiconductors, with a band gap of 1.2 eV
- They have a high optical absorption coefficient, so can be made thin (~2 μm), and have high radiation resistance and reliability
- In-situ HTXRD can be used to investigate synthesis routes



CIGS solar cell structure

HTXRD: Temperature Ramp Anneal



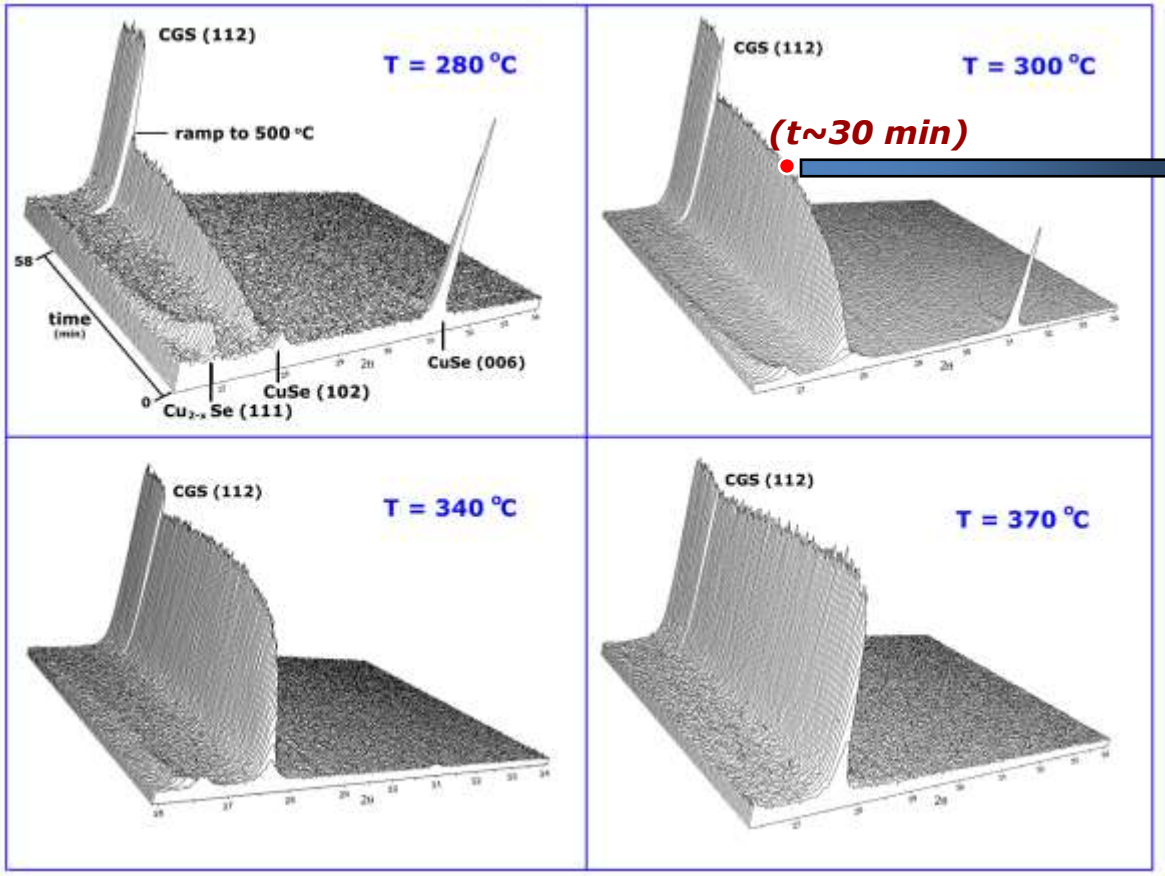


Data collected at HTML using Scintag PADX with mBraun PSD (2 min per 4-part scan) showing intermediate phase during CGS processing
W.K. Kim (U Fla)

Reaction kinetics are suited for study using time-resolved HTXRD

- When coupled with a high-speed data collection system (e.g., high fluxes from rotating anode or synchrotron sources, fast data collection from position-sensitive detectors, etc.), HTXRD enables time-resolved in-situ investigations of the crystalline phases present in real time at high temperature in controlled atmosphere
  - The data collection rate needs to be faster than the rate of change of the sample - may be hours, minutes, seconds, or less!
  - This approach allows for validation of chemical reaction models, and can be used to derive parameters for kinetic reaction-rate models (e.g., Avrami analysis, or other suitable model)

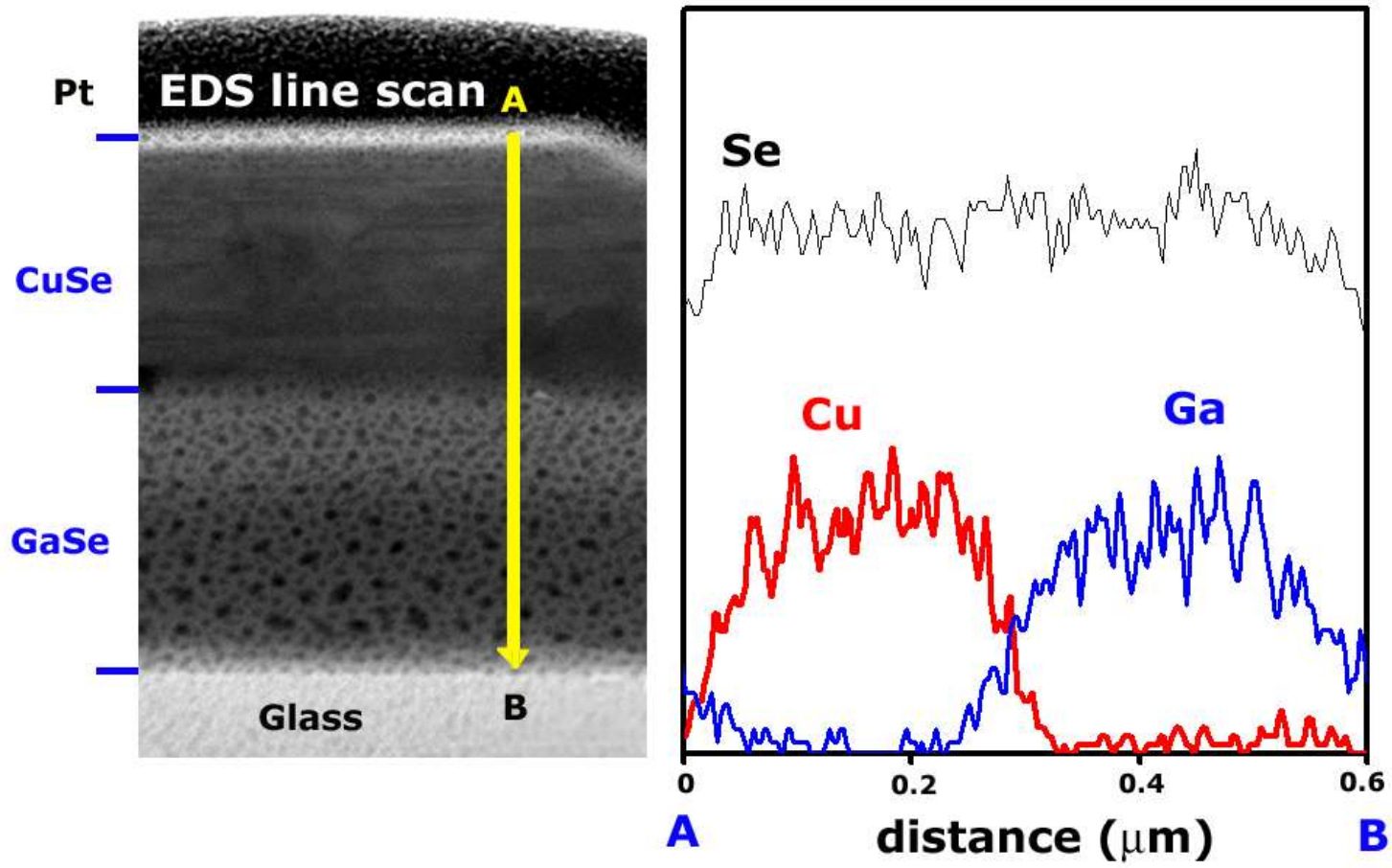
Isothermal annealing



W.K. Kim (U Fla) Thin Solid Films (2007)

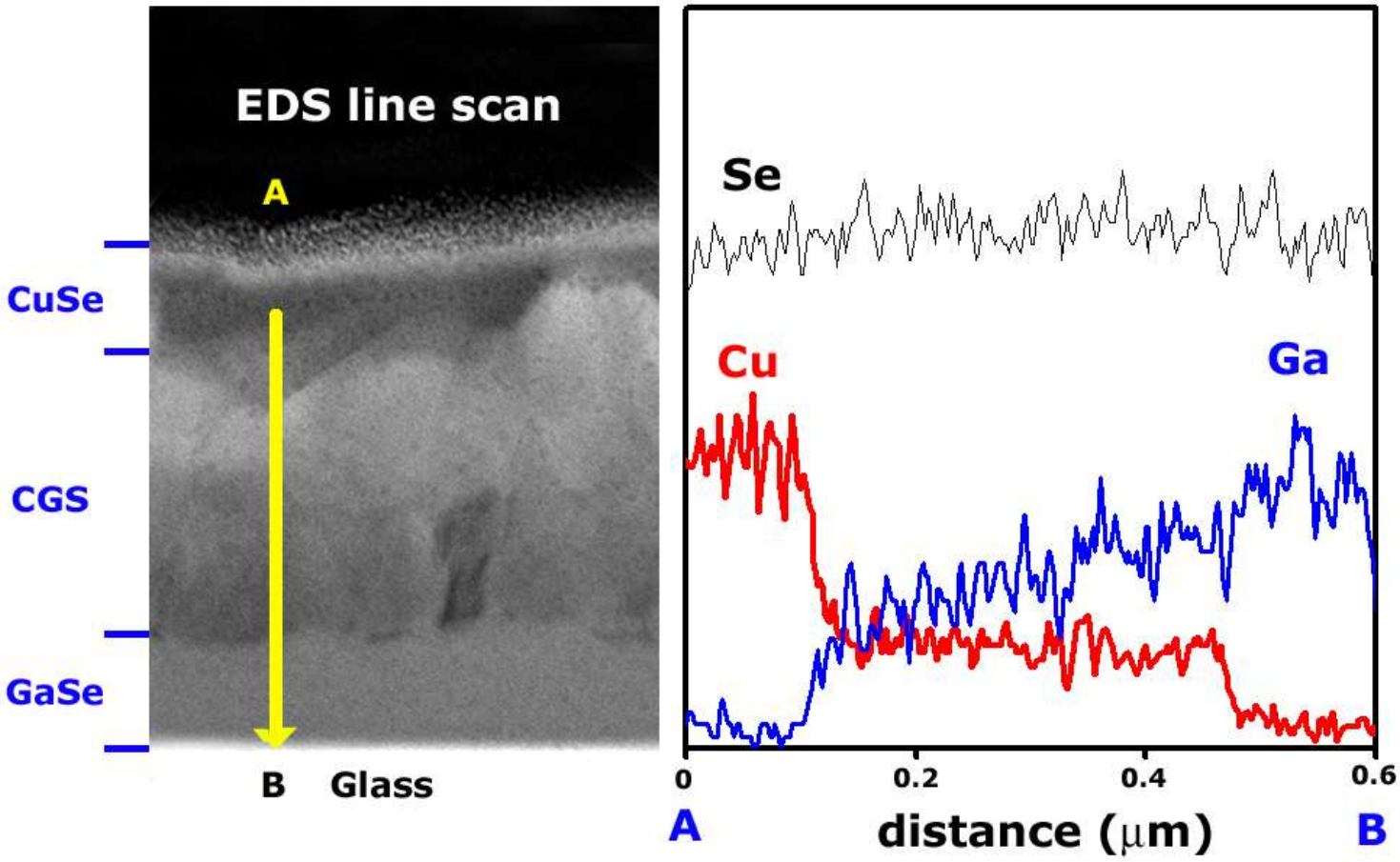
TEM-EDS Analysis

Glass/GaSe/CuSe Precursor



TEM-EDS Analysis

Glass/GaSe/CGS/CuSe annealed for 30 min, at 300 °C



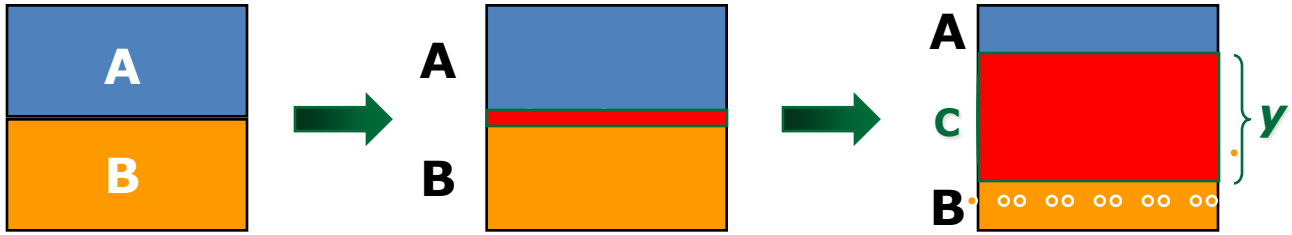
Time-resolved XRD: Obtaining reaction kinetics data

- Determination of rate kinetics requires that data be collected faster than the reaction rate
- If the data is adequate for quantitative phase analysis, then the phase fractions can be measured as a function of time at the non-ambient condition
  - Rietveld-quality data may not be needed – under some circumstances just a single peak can provide quantitative information, and even highly textured polycrystals can be analyzed
- The % transformed as a function of time can be fit to a suitable model to obtain a rate constant (k)
  - The Avrami model is suited for nucleation and growth kinetics
  - The parabolic rate model is better suited for interfacial diffusion
- Analysis of the rate constants for different temperatures in an Arrhenius plot (ln k versus 1/T) yields an activation energy for the reaction.

M.E. Ayturk et al. / Journal of Membrane Science 316 (2008) 97–111

Solid-state Growth Models

- **Parabolic growth model**



Before reaction

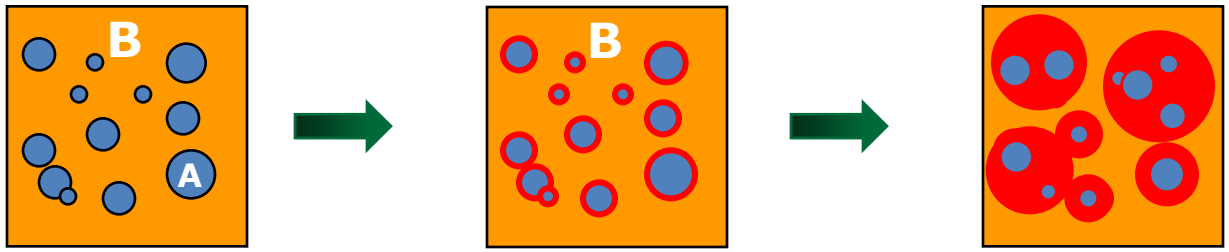
Nucleation at A-B interface

Diffusion thru product & reaction (ex. $D_{BC} > D_{AC}$)

$$\frac{dy}{dt} = \frac{D \cdot k}{y}$$

$$y^2 = k_p \cdot t$$

- **Avrami growth model**



Phase A in matrix B

Nucleation

Diffusion & growth

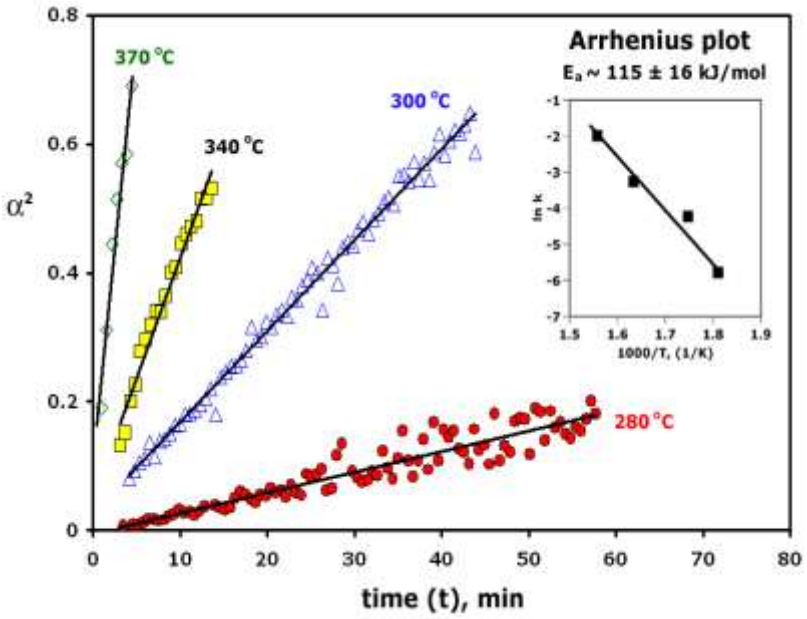
$$x = 1 - \exp[-(kt)^n]$$

$$\ln[-\ln(1-x)] = n\ln t + n\ln k$$

$0.5 < n < 1.5$ (1-D diffusion)

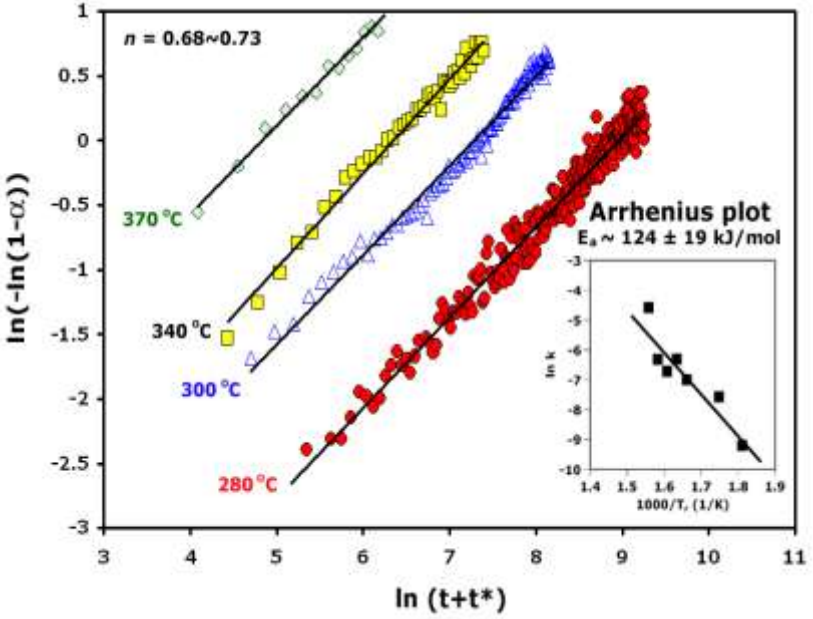
HTXRD: Kinetic Analysis

Parabolic model



$\alpha^2 \sim k \cdot t$

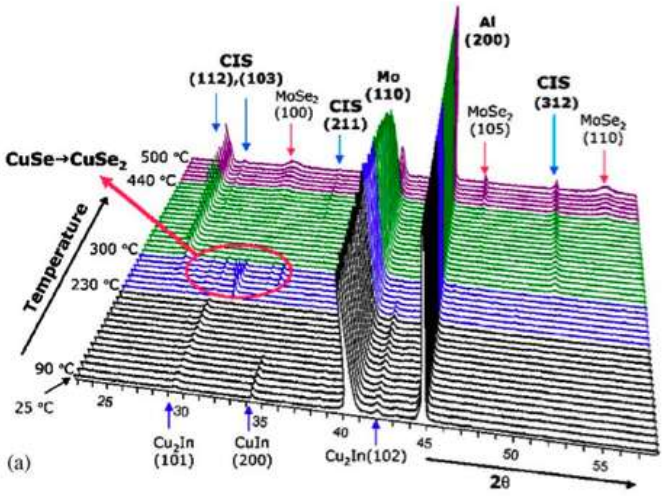
Avrami model

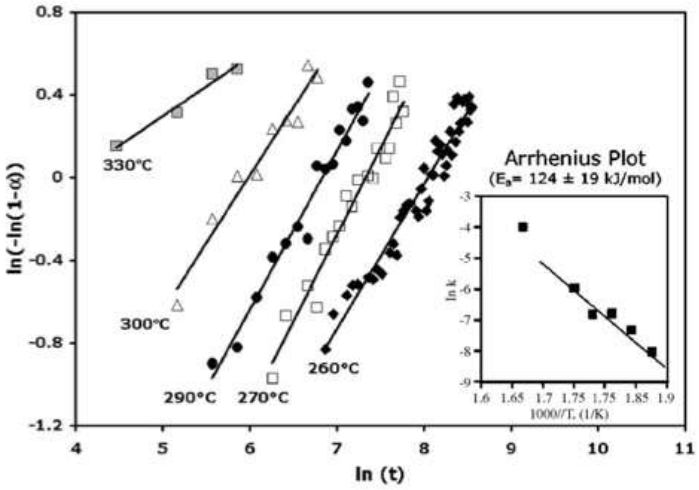


$\ln[-\ln(1-\alpha)] = n\ln(t+t^*) + n\ln k$

➔ Analysis suggests one-dimensional diffusion controlled reaction

Time-resolved in-situ XRD for gas-solid reactions: selenization of CIGS films



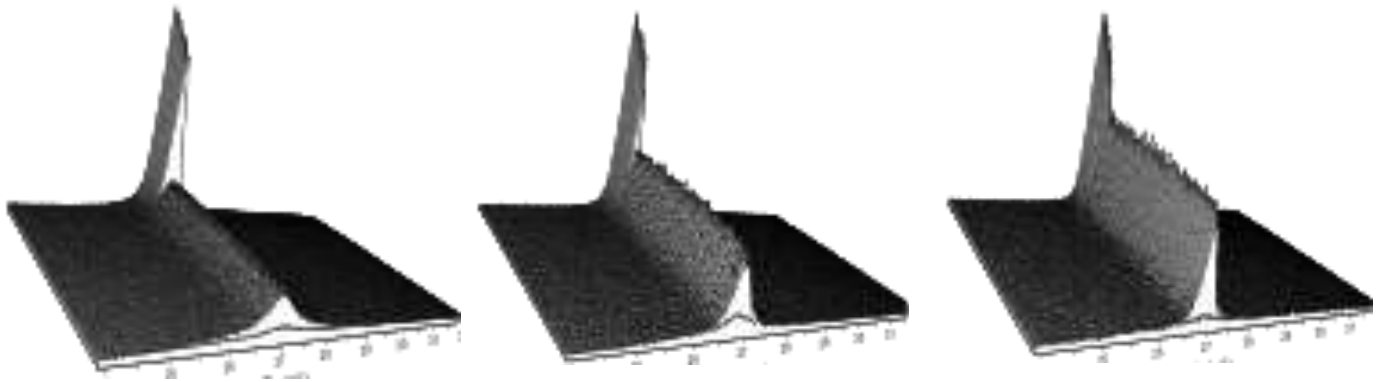


Woo Kyoung Kim (U Florida) J Cryst Growth 2006

•Data taken using a modified Anton Paar XRK900 stage. This sample was a CuIn thin film on a Mo film on a glass substrate. Selenium was introduced as a vapor phase, and the reaction was observed as a function of time and temperature.

•Time-dependent isothermal data at five temperatures were collected. The phase fractions were determined from the peak areas, and fit to a model (typically Avrami or parabolic rate, as appropriate) to determine reaction kinetics information.

In-situ XRD: Temperature dependence of crystallite size



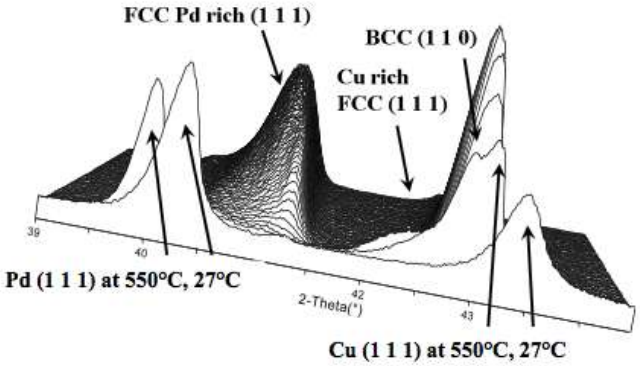
- $CuInSe_2$ (116) peak after heating nanocrystalline precursor at 180, 300, and 350°C for several hours reveals a different (and stable) crystallite size for each temperature
- Final ten scans done at 500°C to achieve similar crystallite size for comparison of data sets

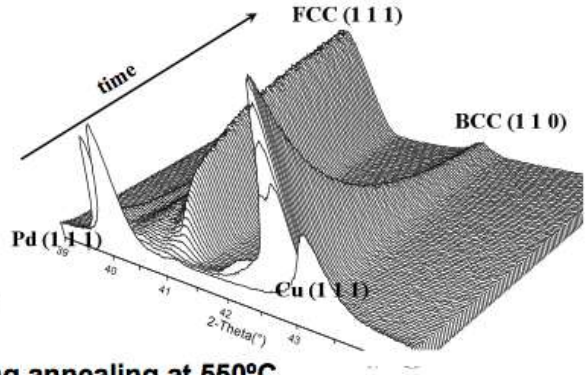
Woo Kyoung Kim (U Florida), unpublished

Alloys for hydrogen separation membranes

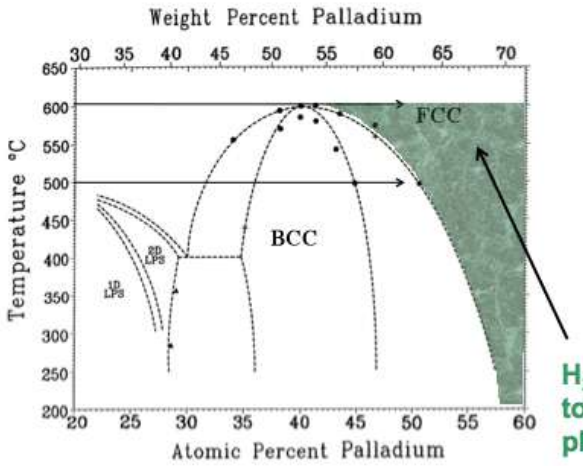
- Palladium membranes are a technology for large-scale hydrogen separation from syn-gas
- Hydrogen diffuses through palladium alloy membranes with 100% selectivity
- Issues:
  - Palladium membrane flux is degraded by sulfur poisoning, but alloying can reduce this issue
  - Membranes need to be thin, so are supported on porous metal or ceramic supports – need to consider interfacial reactions
  - Large lattice dilation at low temperatures due to formation of metal hydrides

In-situ XRD for reaction pathways and kinetics: Pd-Cu alloy formation



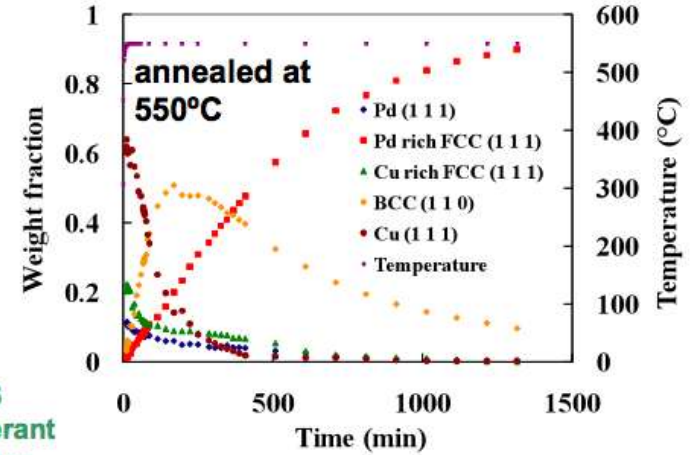


XRD patterns during annealing at 550°C.



Pd - Cu phase diagram [2].

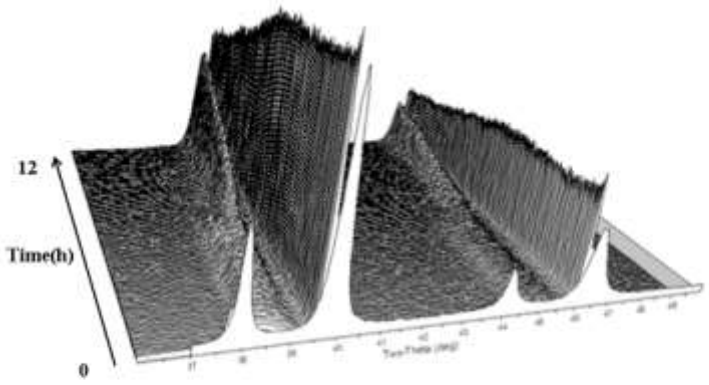
H_2S tolerant phase



Weight fractions were calculated with the direct comparison method [3].

- Natalie Pomerantz (WPI), AIChE Journal (in press)

Reaction pathways for Pd-Au are quite different from Pd-Cu



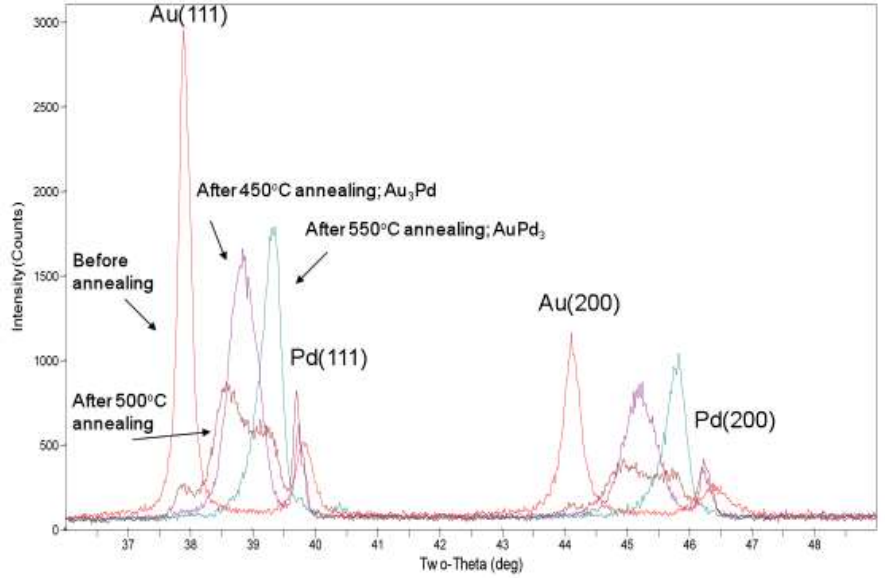
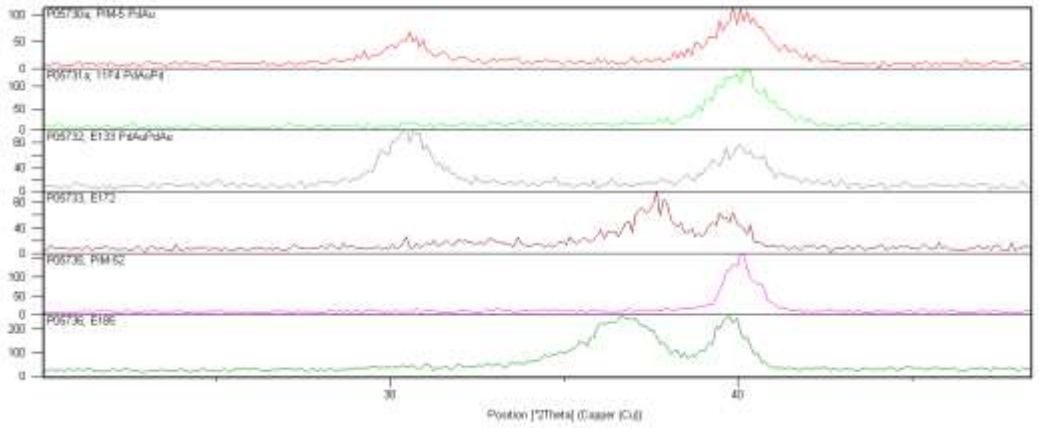


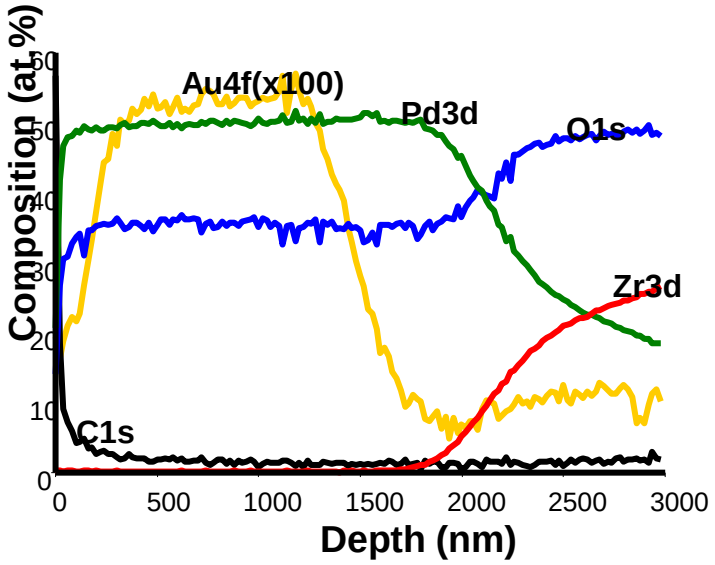
Fig. 1: An example of high-temperature x-ray diffraction data set, which displays a series of isothermal x-ray scans of a Au-Pd bi-layer film as a function of time (In this example, the isothermal temperature is 500°C in helium environment).

- Pd-Au has thermodynamically favored ordered compositions at Au_3Pd and $AuPd_3$
- These ordered phases impact the diffusion constants
- Chao-Huang Chen (WPI) unpublished

H_2 Separation Membranes: Phase distribution in Pd-Au alloys

- XRD results suggested that these Pd-Au alloys were two-phase, and subsequent XPS confirmed and located the two alloy phases





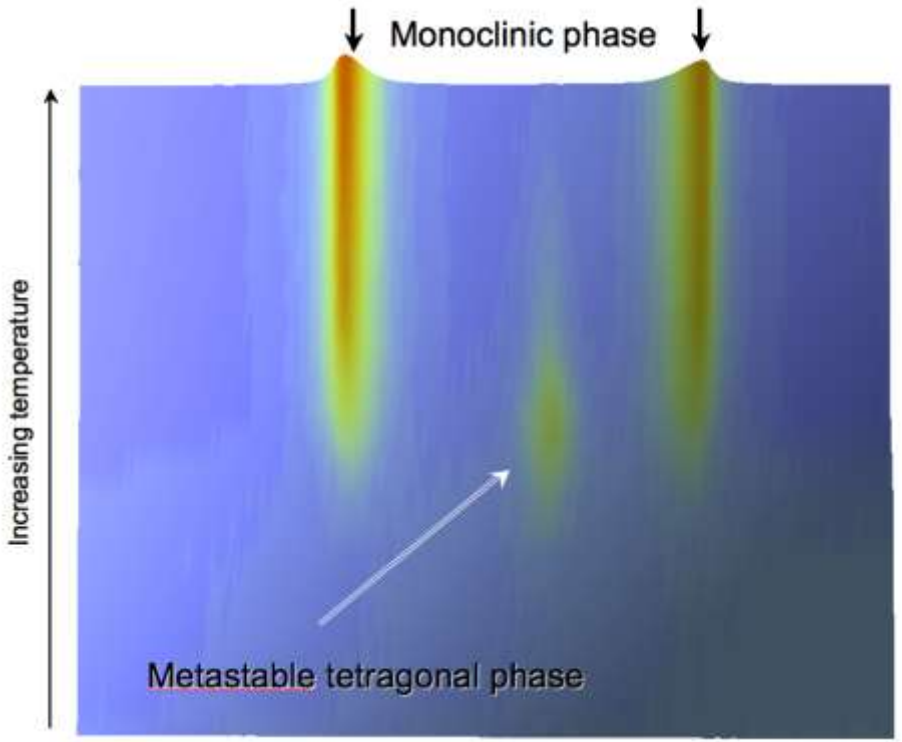
XPS data by Dr. Harry Meyer, III (HTML)

High-κ dielectric materials

- Silicon dioxide has been used as a gate oxide material for decades
- As transistors have decreased in size, the thickness of the silicon dioxide gate dielectric has steadily decreased to increase the gate capacitance and thereby drive current and device performance
- At thicknesses below 2nm, leakage currents due to tunneling increase and impact performance
- Hafnium oxides are of great importance to the semiconductor industry as high-κ gate dielectrics to replace silicon oxynitrides
- In-situ HTXRD can be used to study crystallization of HfO_2 films from amorphous precursor

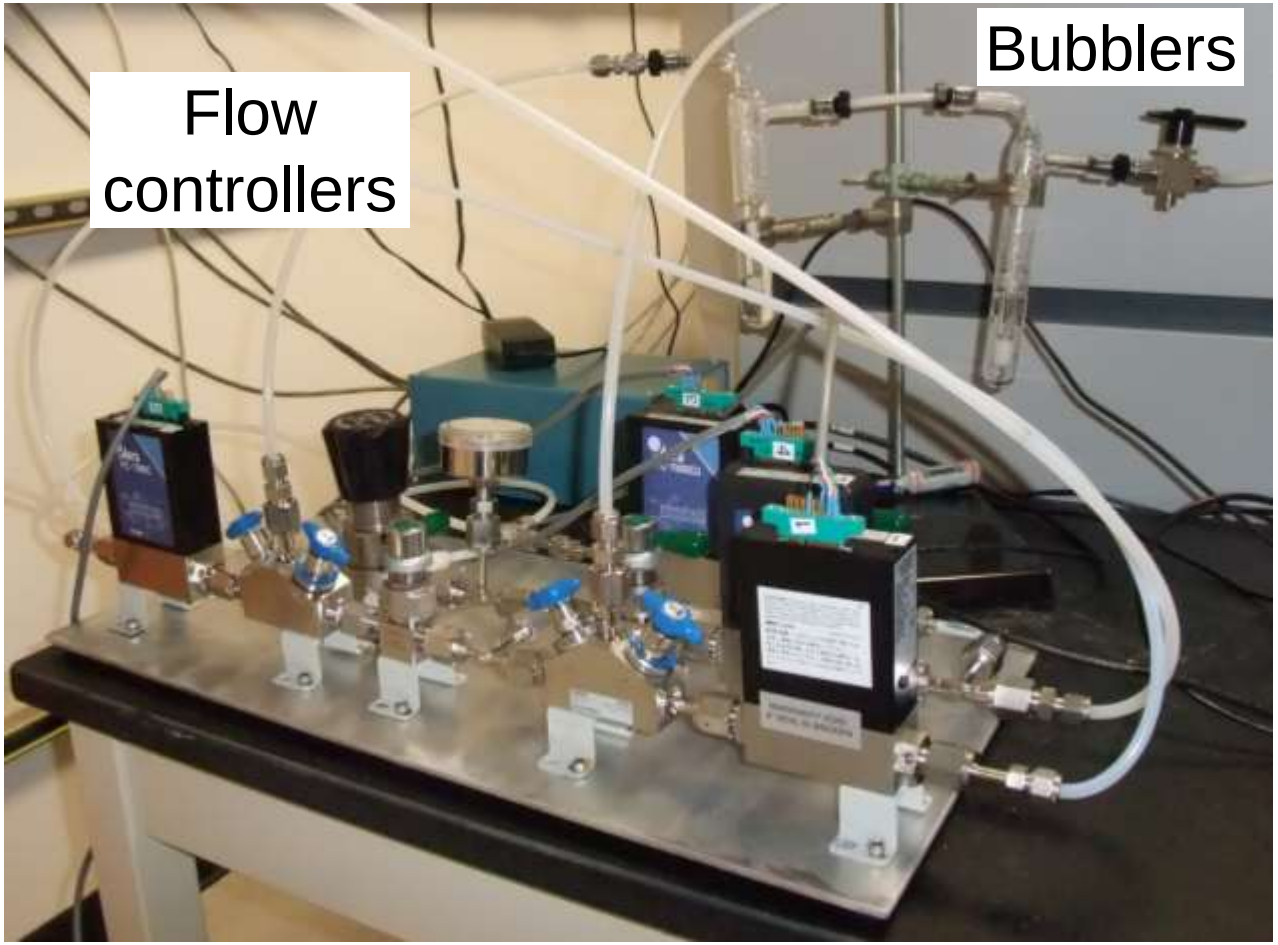
In-situ Crystallization Study: HfO_2

- The first crystalline phase to form is the tetragonal (cubic?) phase, even though this is well below the temperature required for this phase in bulk material.
- The tetragonal (cubic?) phase is transient, and is rapidly replaced by the stable monoclinic phase
- A similar crystallization path has been noted for isostructural ZrO_2



Catriona McGilvery (Imperial College), J.Amer. Cer. Soc. (in press)

More specialized gas systems can be incorporated as needed



Stephanie Sorenson (Univ Colorado), J Membr Sci (2010)

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Center for Nanophase Materials Sciences

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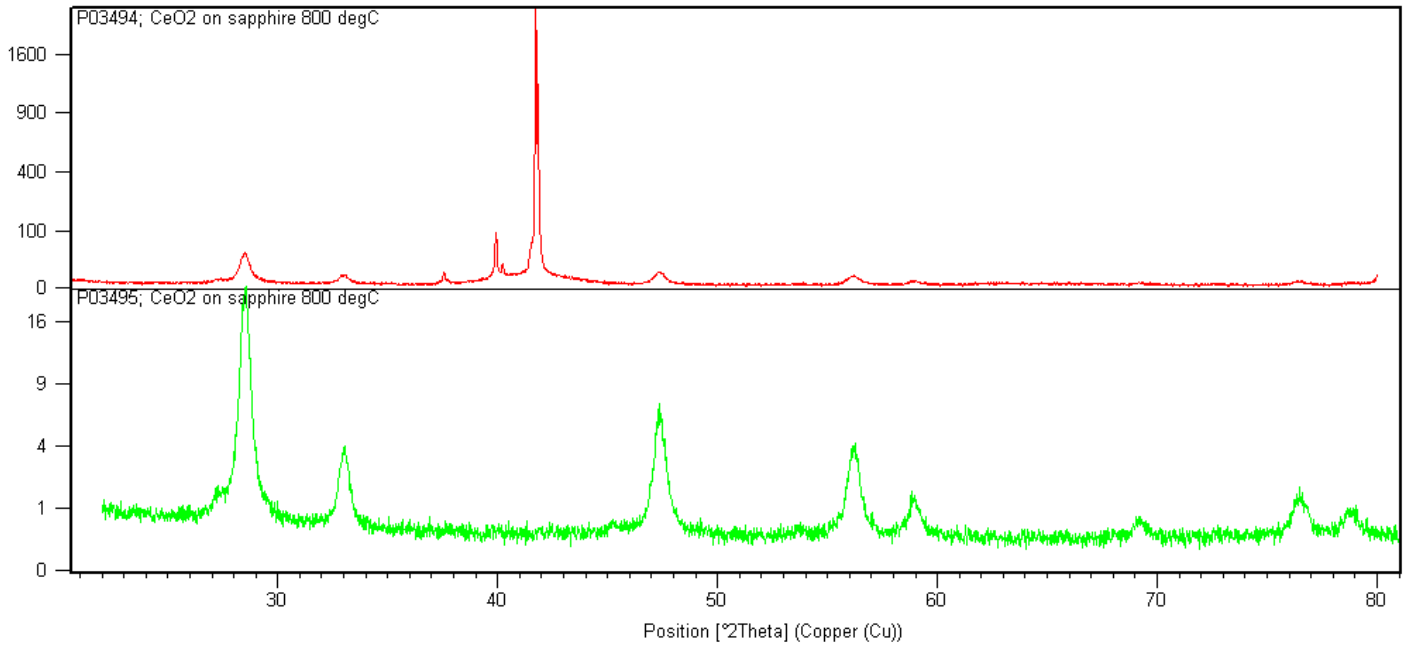
Single crystal substrates can dominate the pattern



- **Solution (for polycrystalline films) is to tilt the sample just a few degrees to eliminate the substrate peaks, as shown above (cerium oxide on sapphire)**