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Crystallization Kinetics and Microstructure Evolution of Vapor-Deposited Hexanitroazobenzene (HNAB) Films

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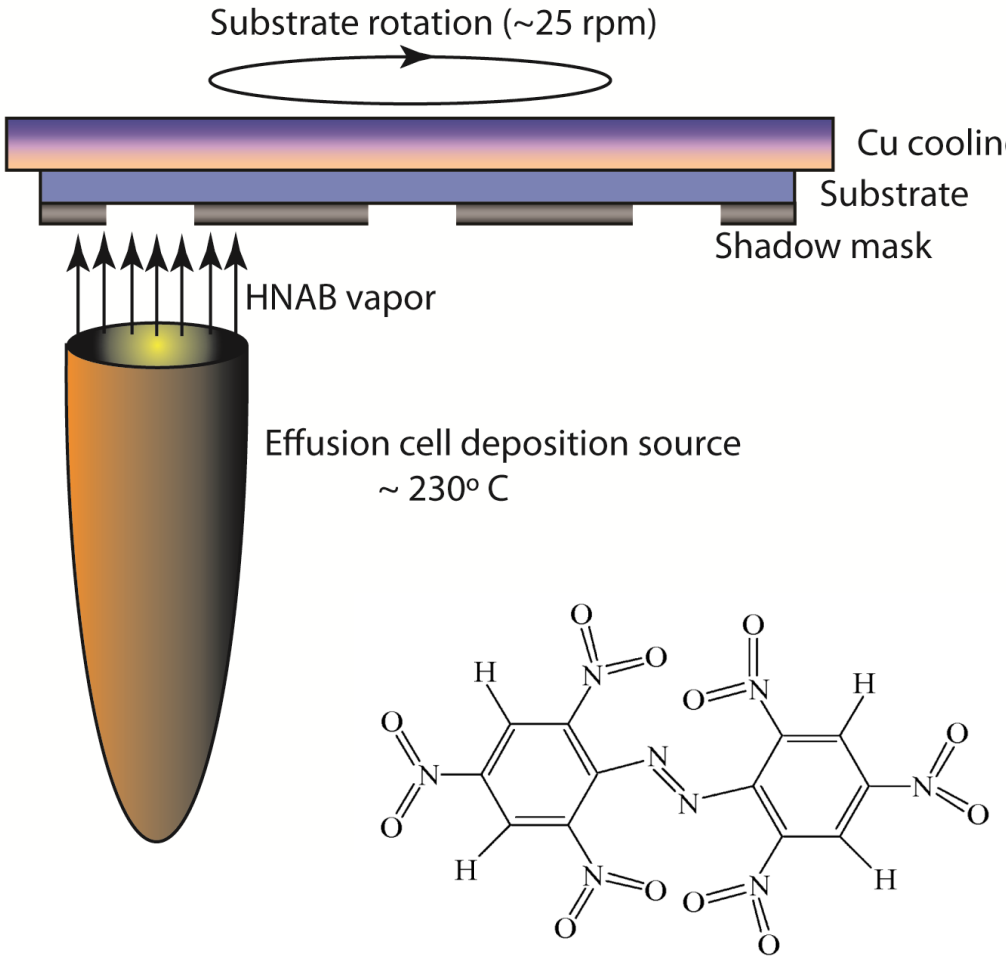
Motivation

- **Vapor-deposited hexanitroazobenzene (HNAB) is an interesting material for studying explosive behavior at sub-mm geometries**
  - Relatively small critical thickness for detonation to propagate (< 200 μm)
  - If substrate is kept sufficiently cool, deposition leads to a dense (non-porous), amorphous structure – independent of substrate or small variations in deposition conditions

- **Amorphous structure is not stable**
  - At RT, crystallization occurs over several weeks – faster at elevated temperatures
  - Effects of temperature on morphology and crystallization kinetics?

Film Deposition



- Base pressure ~10^{-6} Torr
- (100) Si substrates
- 10 mm source-substrate distance
- ~100 μm thick films after 30 minute deposition

Schematic of deposition from effusion cell source and molecular structure of HNAB

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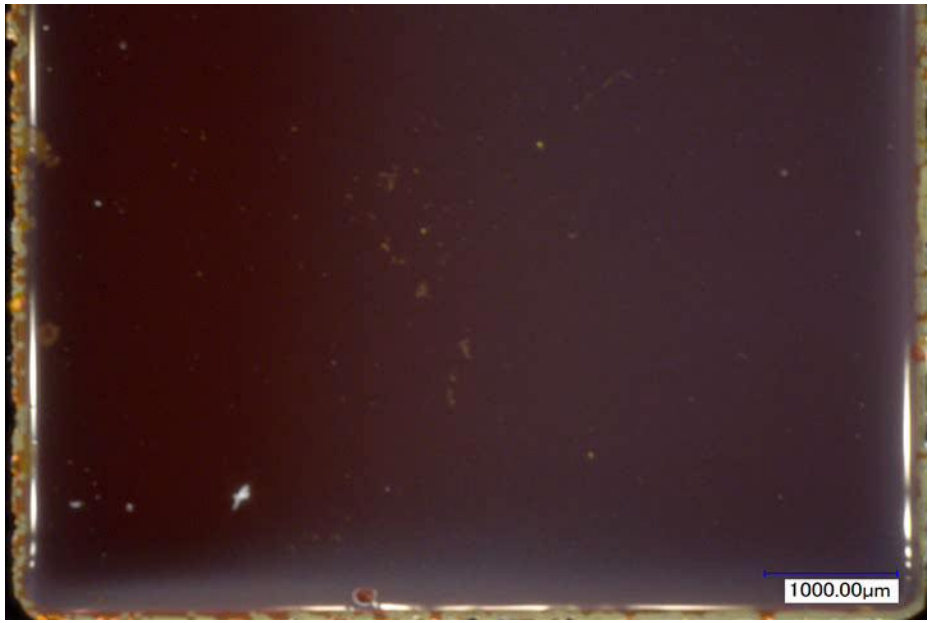
Time-Lapse Optical Microscopy (RT–65ºC)



Time-lapse video of crystallization at 40ºC
1.5 hour time-lapse, 3.5 days elapsed

Time-lapse video of crystallization at 65ºC
1.5 min time-lapse, 2.5 hrs elapsed

- Similar nucleation and growth process at temperatures 65ºC and below
  - ⇒ Orange regions = HNAB-II, Yellow = unknown polymorph
  - ⇒ Higher temperatures lead to faster crystallization
  - ⇒ Greater amount of HNAB-II with increasing temperature

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Time-Lapse Optical Microscopy (75ºC)

Time-lapse video of crystallization at 75ºC
15 sec (initial darkening)/2 min time-lapse,
2 hrs elapsed

- Initial surface darkening observed at temperatures above 70ºC
- Leads to very different crystallization behavior, progressing primarily from the edges towards the center and forming primarily the unknown polymorph
- Onset of darkening delayed by heating in flowing Ar atmosphere

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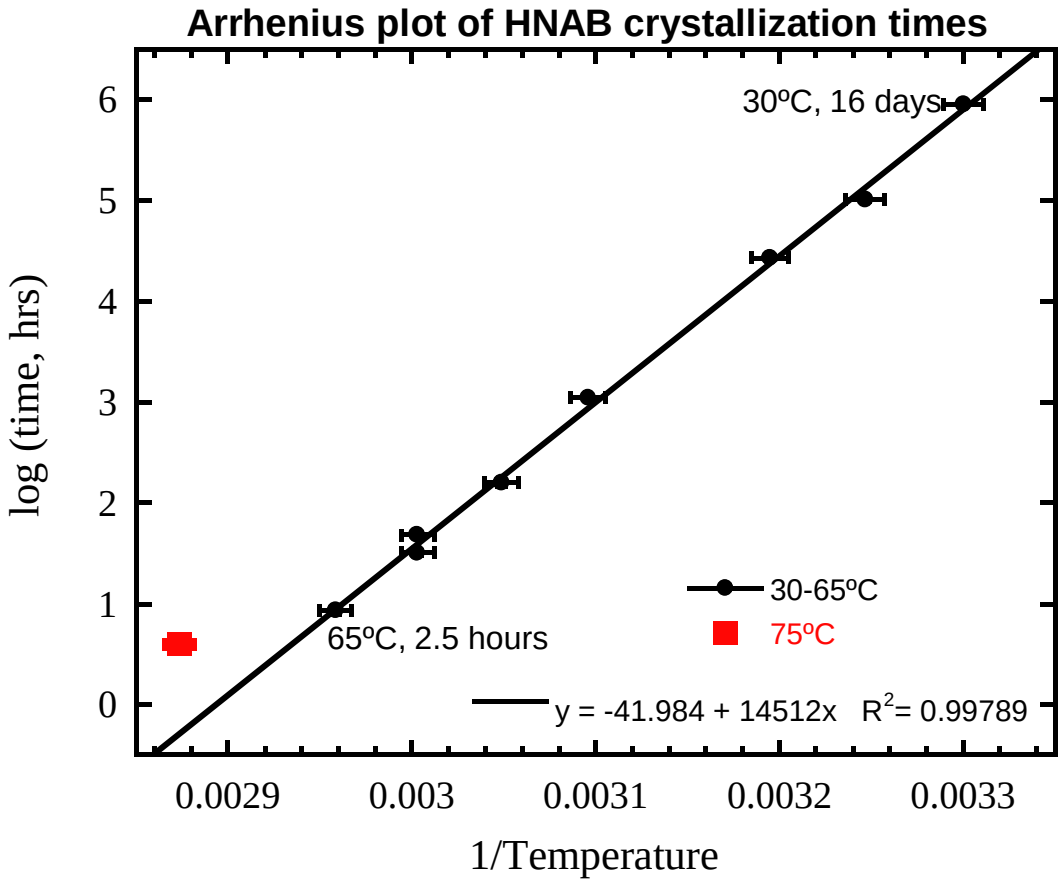
Crystallization Kinetics

- Despite variation in spatial distribution of nucleation sites, time for complete crystallization falls on an Arrhenius plot
- Linear fit appears to be valid for temperatures ≤ 65ºC (prior to surface darkening)
- Crystallization rate inhibited at higher temperatures (where surface darkening occurs)
- Extrapolates a crystallization time of ~8 years at 0ºC



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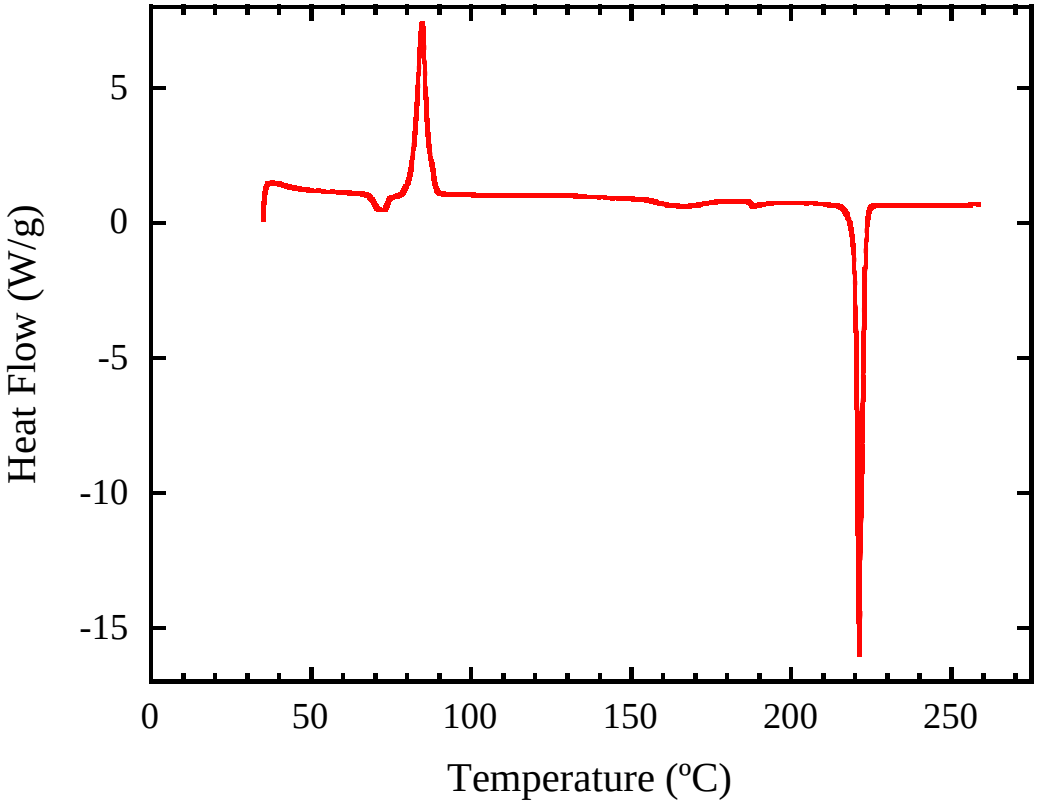
DSC Analysis

- Suggests that glass transition occurs at ~70ºC
  - ⇒ Same temperature as the onset of surface darkening
- Crystallization exotherm occurs shortly after T_g
  - ⇒ Heat of crystallization ~55 J/g
- Large melting endotherm at 221ºC, consistent with literature
- Smaller endotherms at ~166 and 188ºC attributed to polymorphic changes



DSC data from an amorphous HNAB film heated from 40−250ºC at 5ºC/min.

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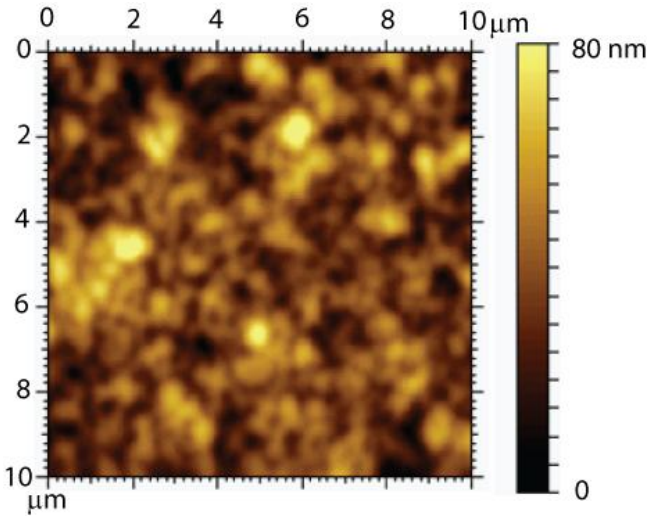
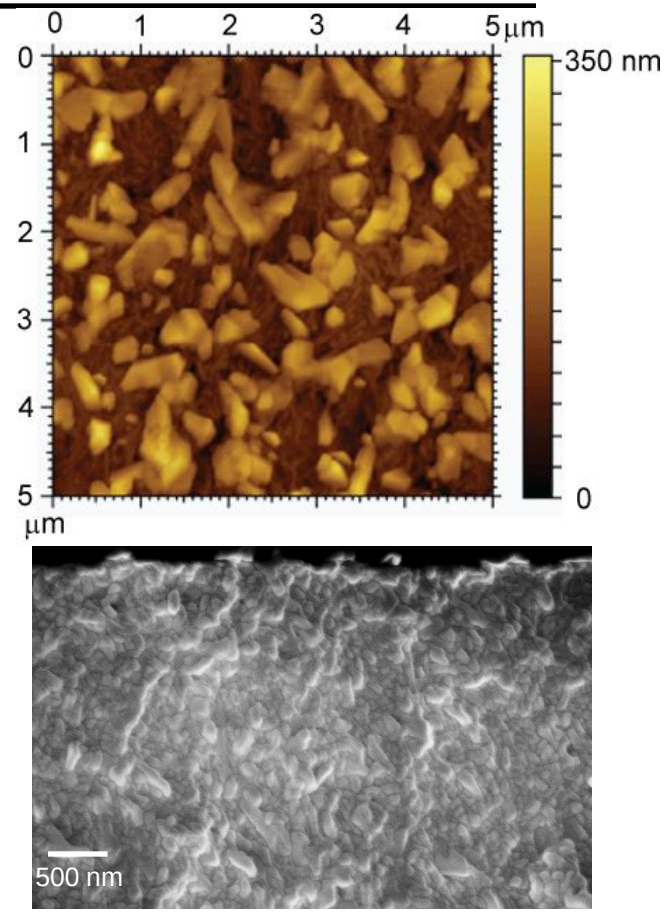
Microstructure Evolution – Low Temperature



AFM image of an as-deposited amorphous HNAB film



AFM and SEM images following crystallization at 60ºC

- Crystallization at temperature has only small effects on resultant microstructure below 65ºC
- Surface roughness increases from ~15 nm to 50 nm during crystallization
- Grain size after crystallization below 65ºC ~100 nm

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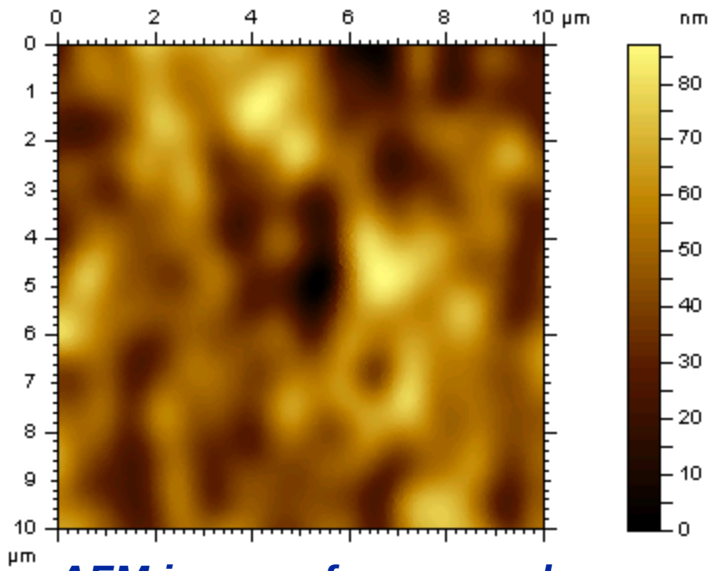
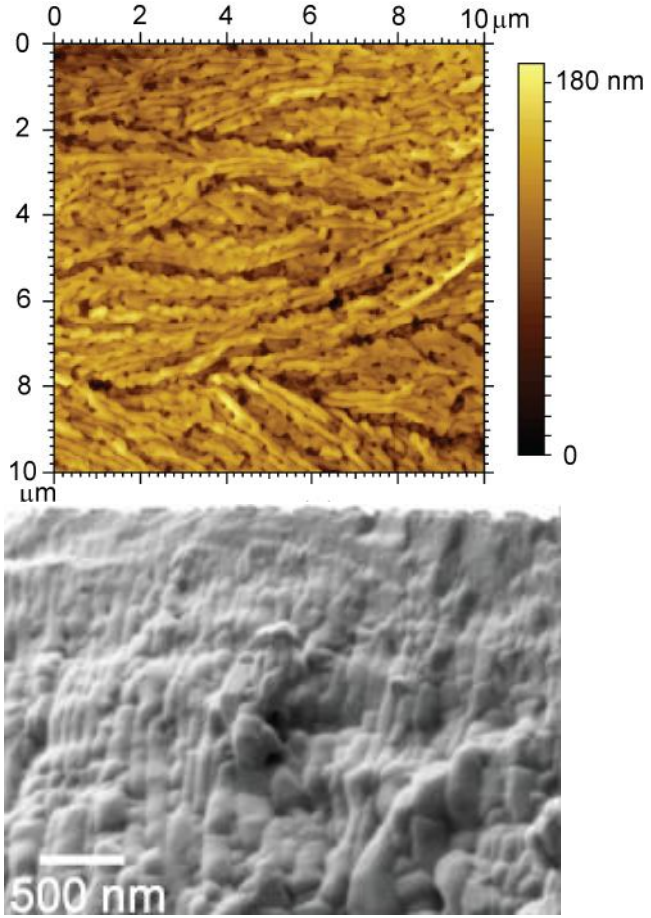
Microstructure Evolution – Higher Temperatures



AFM image of an amorphous HNAB film after heating to 75ºC



AFM and SEM images following crystallization at 75ºC

- Major changes in microstructure of crystallized HNAB observed at temperatures above 70ºC
- Smoother, vermicular surface morphology (~25 nm surface roughness)
- Larger grain size in interior of film (~300nm – 1µm)

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Conclusions

- Vapor-deposited HNAB films form a dense amorphous structure that crystallizes over time to a mixture of HNAB-II and an unknown crystal structure
- At temperatures below ~70ºC, crystallization times follow an Arrhenius behavior and microstructure varies only slightly with crystallization temperature
- At higher temperatures, surface darkening leads to…
  - A different polymorph becoming dominant
  - A very different surface morphology evolving
  - A substantial decrease in the rate of crystallization

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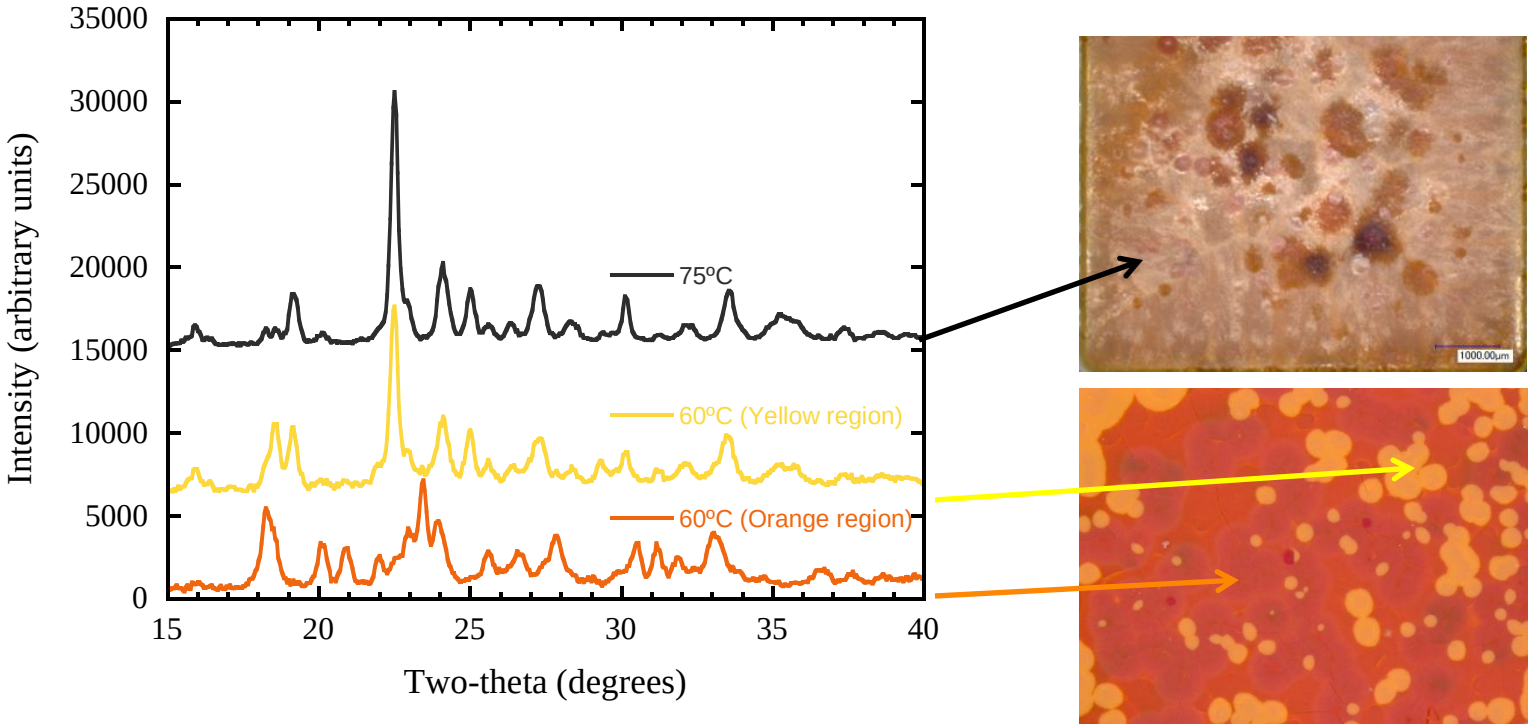
Bonus Slides

X-ray Analysis – Phase Identification



- Regions of different colors isolated using GADDS with 300 μm spot size
- Film at 75ºC – Not identified, large peaks match HNAB-III, but others do not
- Film at 60ºC –
  - Orange regions consistent with HNAB-II
  - Yellow regions very similar to film crystallized at 75ºC

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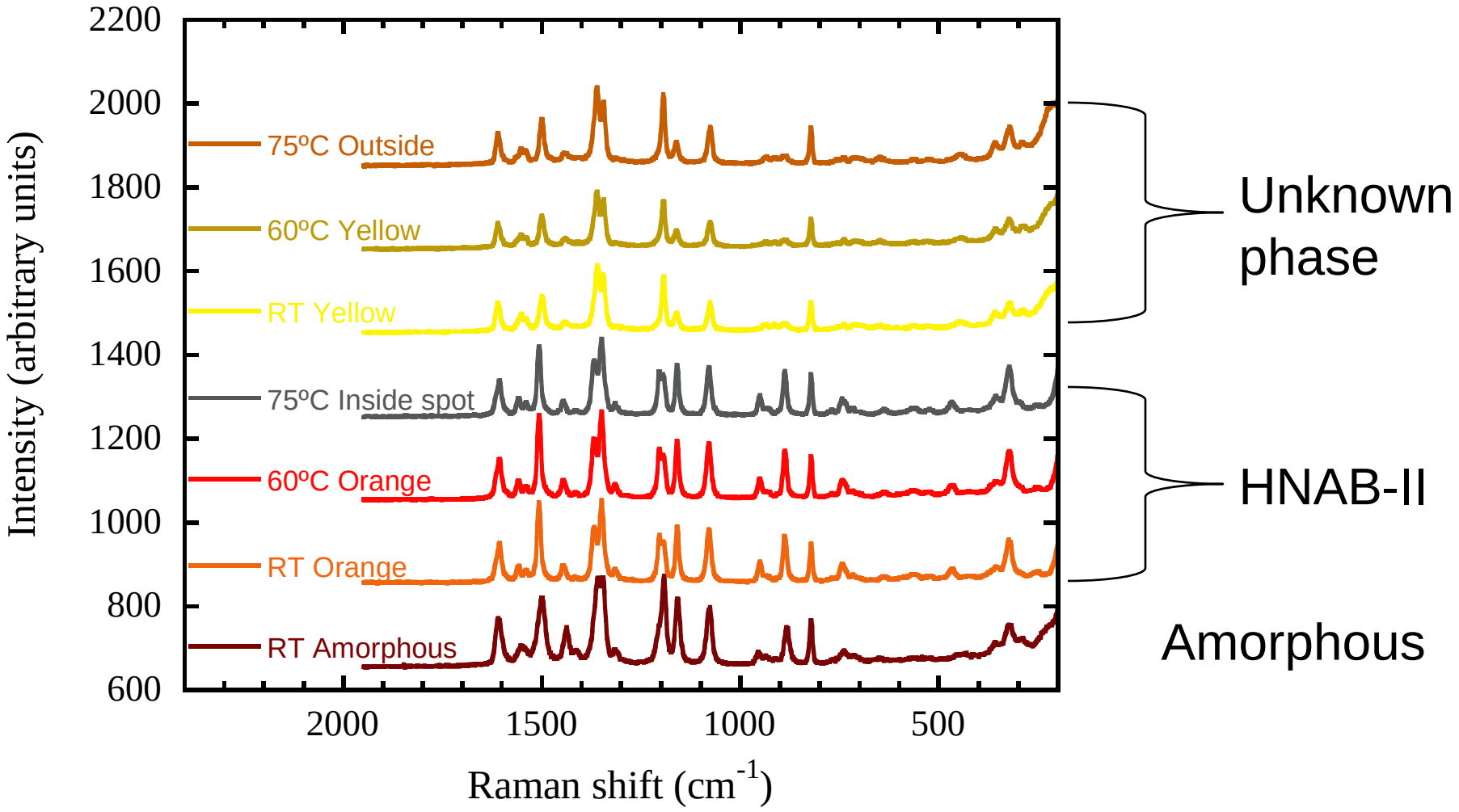
Raman Analysis – RT, 60ºC, and 75ºC



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Future Work

- **Isolate/identify unknown crystal structure**
- **Further kinetics experiments**
  - Crystallization front velocity for each phase
  - Activation energy for crystallization of each phase
- **Effects of microstructure on explosive properties?**
  - Detonation velocity
  - Critical thickness for detonation

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