Creating Durable Chalcogenide Glasses With Controlled Crystallization

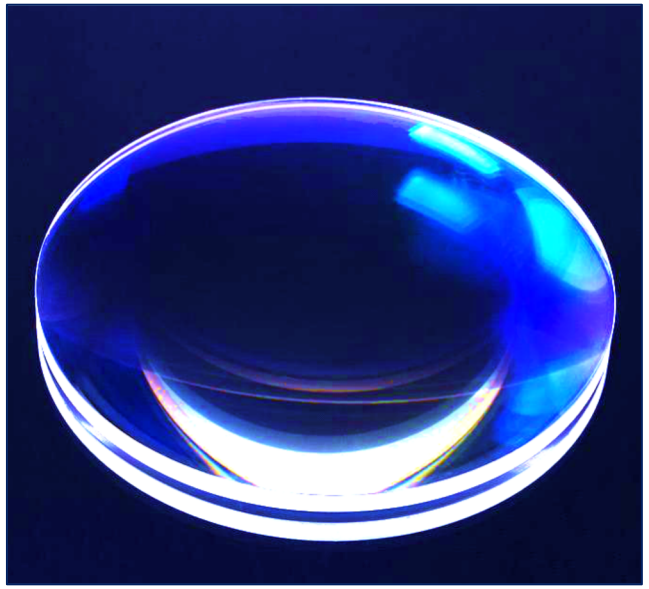
Rebecca Welch[1*], Rashi Sharma[2], The OML Crew[2], Kathleen Richardson[2], Mario Affatigato[1]

[1]Department of Physics, Coe College, Cedar Rapids, IA

[2]CREOL, Center for Optics and Photonics, University of Central Florida, Orlando, FL

Chalcogenide glasses

- Transmission in infrared (IR) wavelength
- Wide range of applications including
  - Optical fibers
  - Lenses
  - Sensors



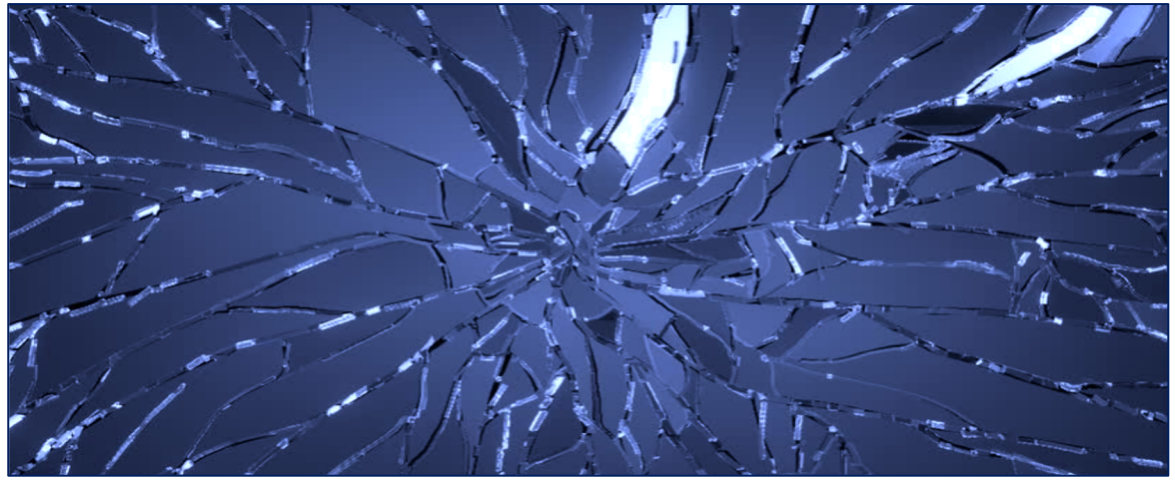
Chalcogenide glasses

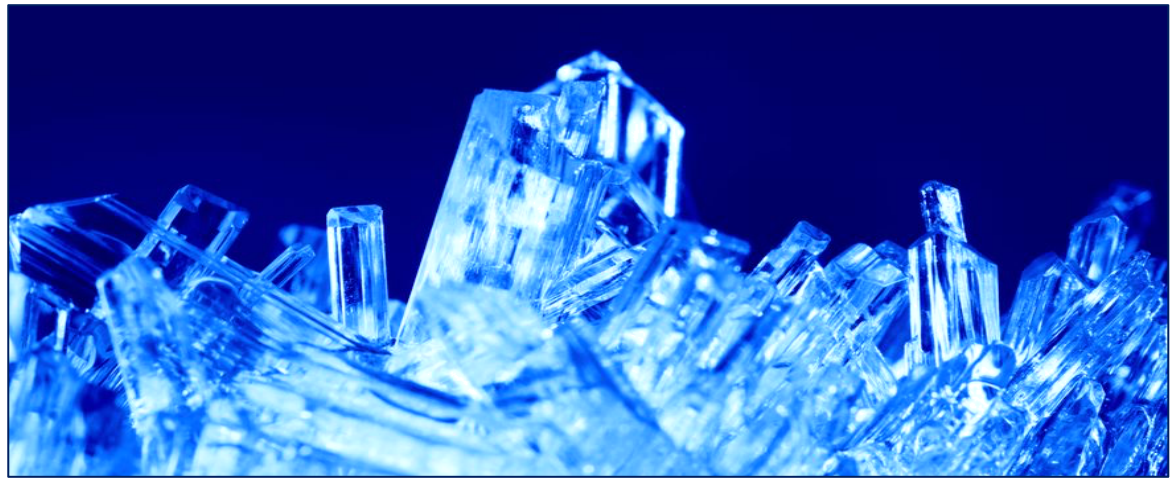
However…

- Very brittle
- Poor chemical durability

Creating crystals would solve this which leads to the creation of a *glass ceramic*.

Must be careful though! Crystals cause the loss of transmission.



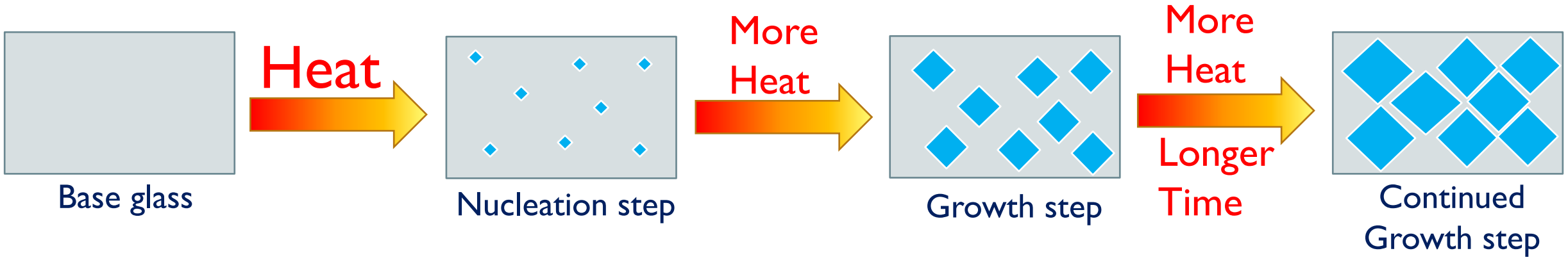


Glass Ceramics

A glass ceramic is created when the glass undergoes *timed* heat treatments to allow the development of crystals.

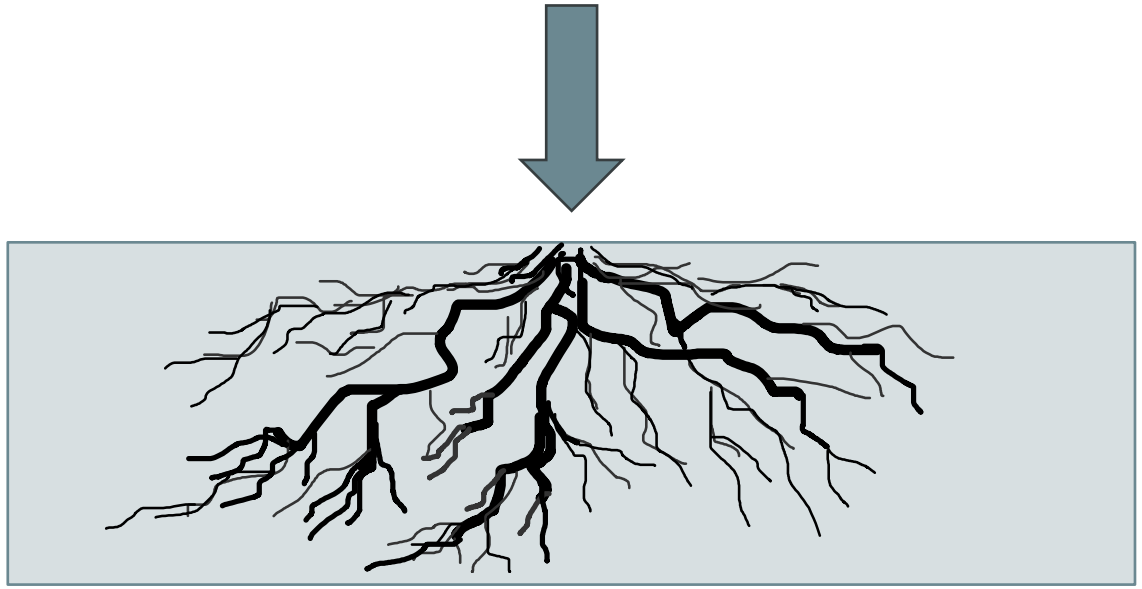
Glass ceramics are stronger than glass due to:

- Uniform particle distribution
- Little porosity

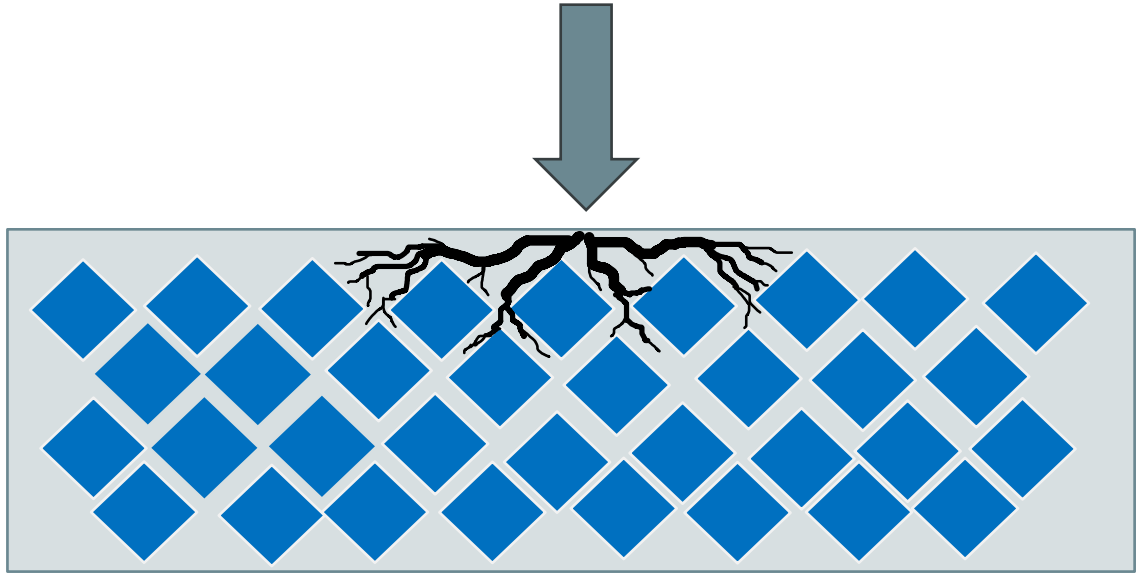


Glass Ceramics

Also have a higher fracture toughness because fracture fronts are forced to go around the crystal.



Traditional glass surface when exposed to a fracture-causing force.



Glass ceramic version when exposed to same force.

Glass Ceramics

Even more importantly…

Crystal growth allows for tailorable refractive index by controlling the volume fraction of the crystals and the glass!

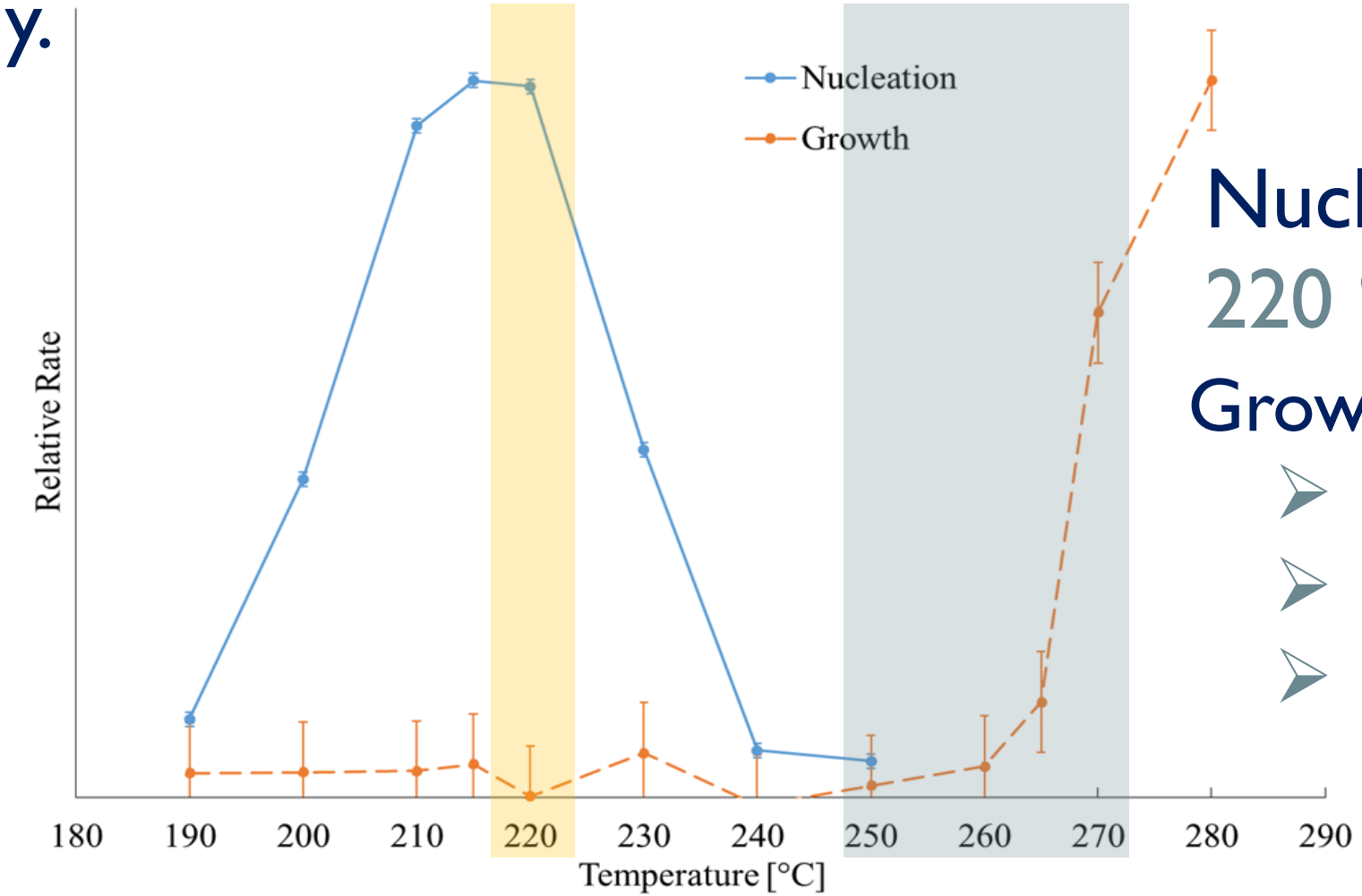
$$n_{eff} \approx (V_{glass})(n_{glass}) + (V_{crystal})(n_{crystal})$$

But more crystals also leads to less transmission due to:

- Scattering – due to crystals
- Absorption – natural loss from glass & from crystals
- Fresnel loss – surface reflection

The GAP-Se Chalcogenide Glass

$20GeSe_2$-$60As_2Se_3$-20PbSe has been used in heat treatments previously.



Nucleation step:

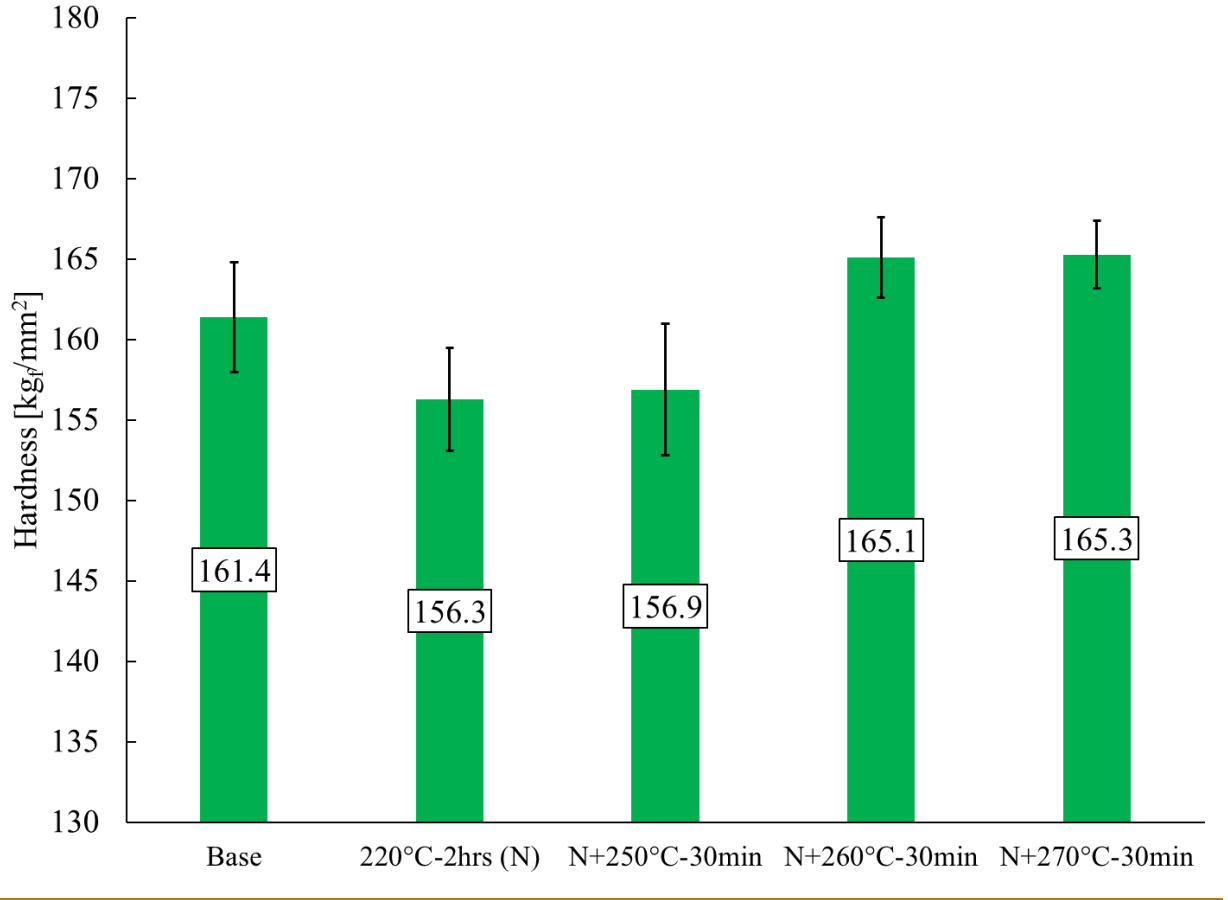
220 °C for 2 hours

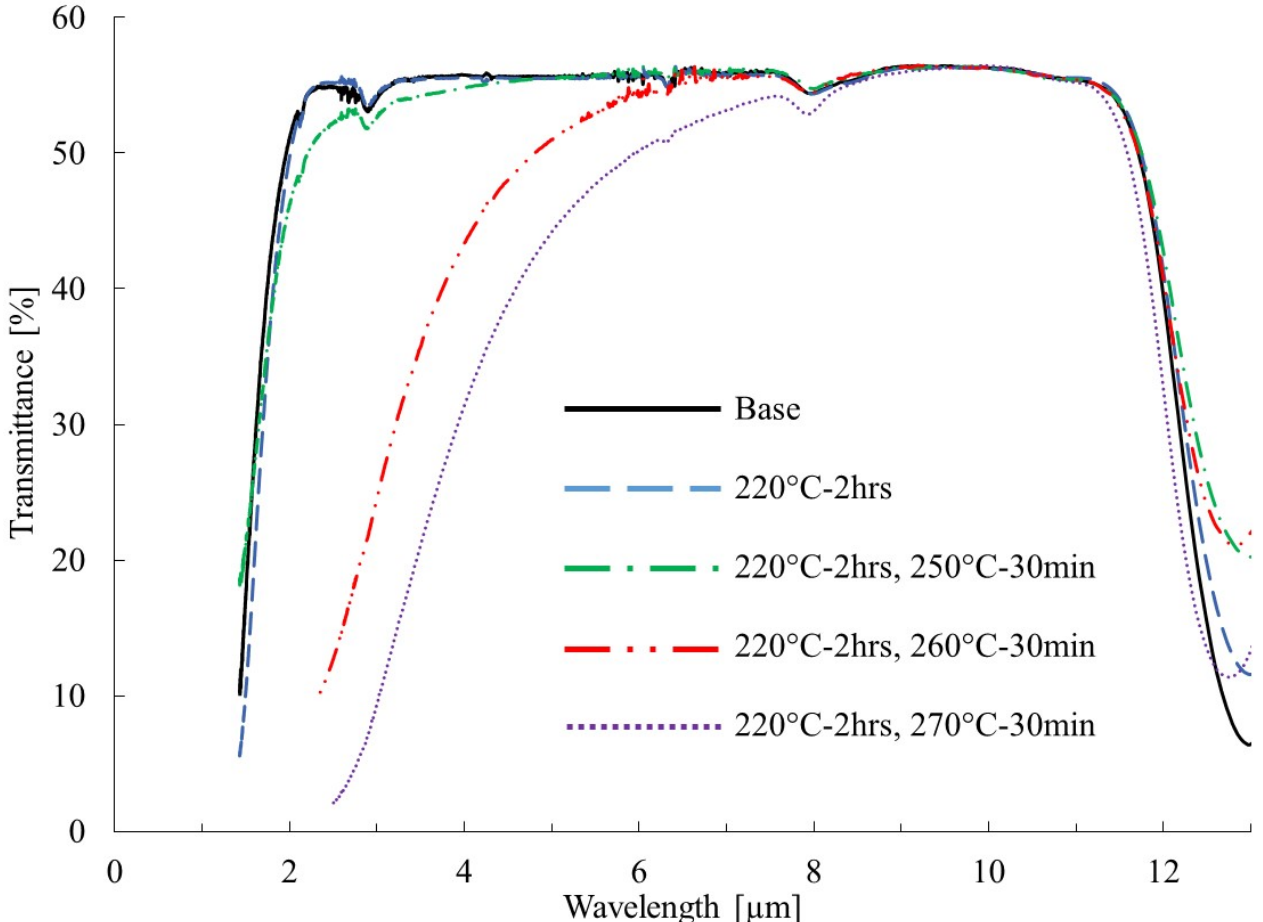
Growth step (30 mins):

- 250 °C
- 260 °C
- 270 °C

The GAP-Se Chalcogenide Glass

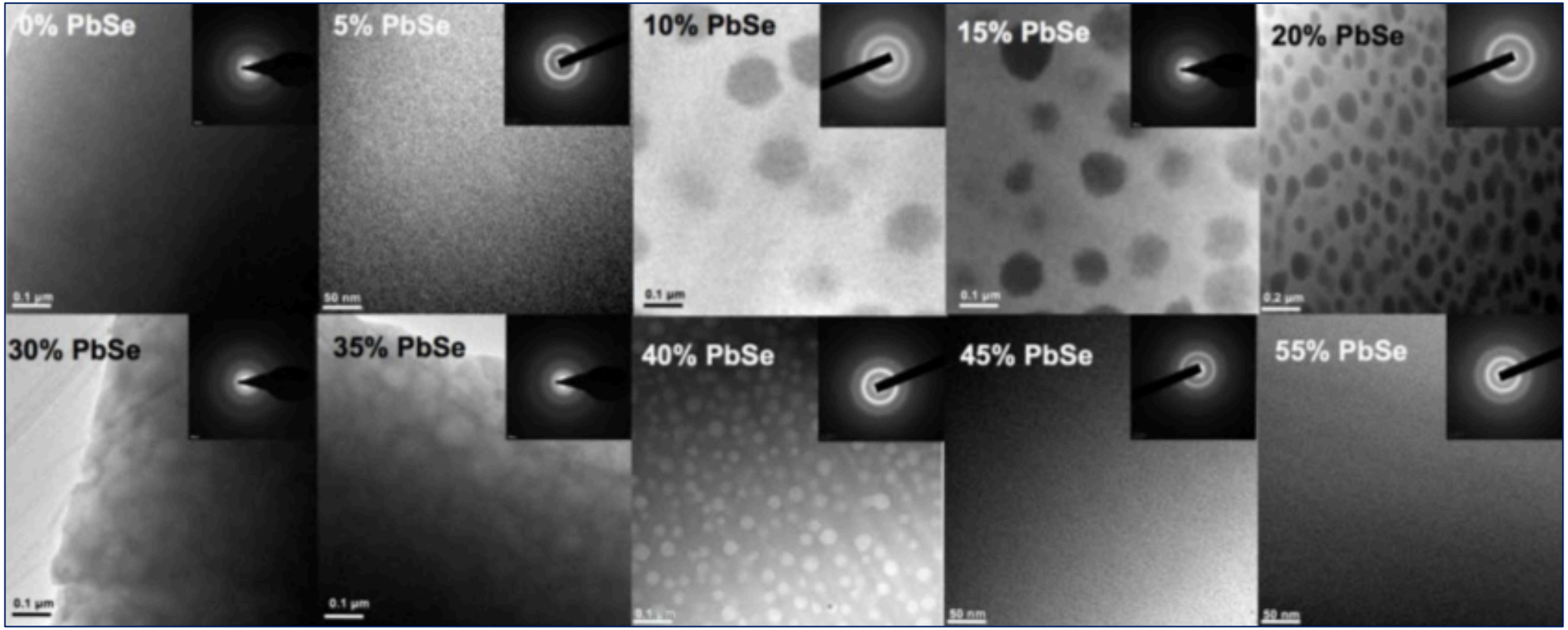
Heat treatments led to little increase in hardness with high scattering.





The GAP-Se Chalcogenide Glass

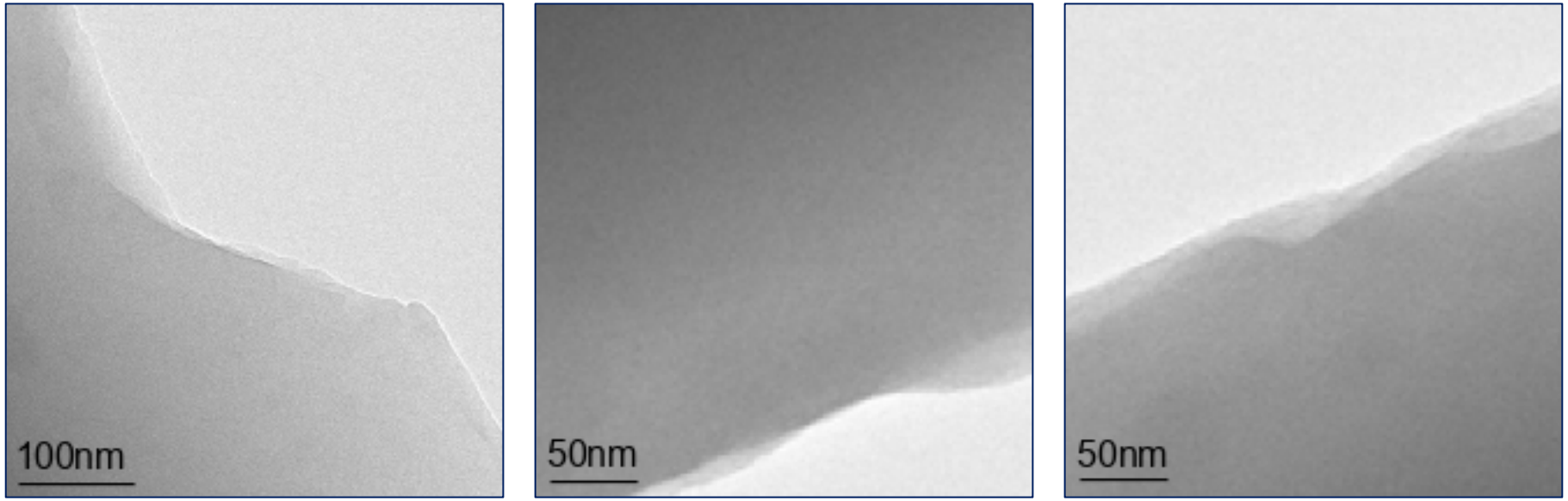
Heat treatments caused more scattering due to the glass's phase separation.



Transmission Electron Microscopy (TEM) images of GAP-Se glass.

The New GAP-Se Chalcogenide Glass

New glass versions created by Amorphous Materials Inc. (AMI) are completely homogenous!



Transmission Electron Microscopy (TEM) images of AMI samples collected by Dr. Kang

Purpose & Methods

See if these new glasses can undergo crystallization, leading to a more durable material with low optical losses.

1. Use heat treatments to create crystals.
2. Observe crystal growth with SEM & XRD
3. Measure Vicker's hardness of the glass.
4. Measure density.
5. Measure transmission with FTIR.

Heat Treatments

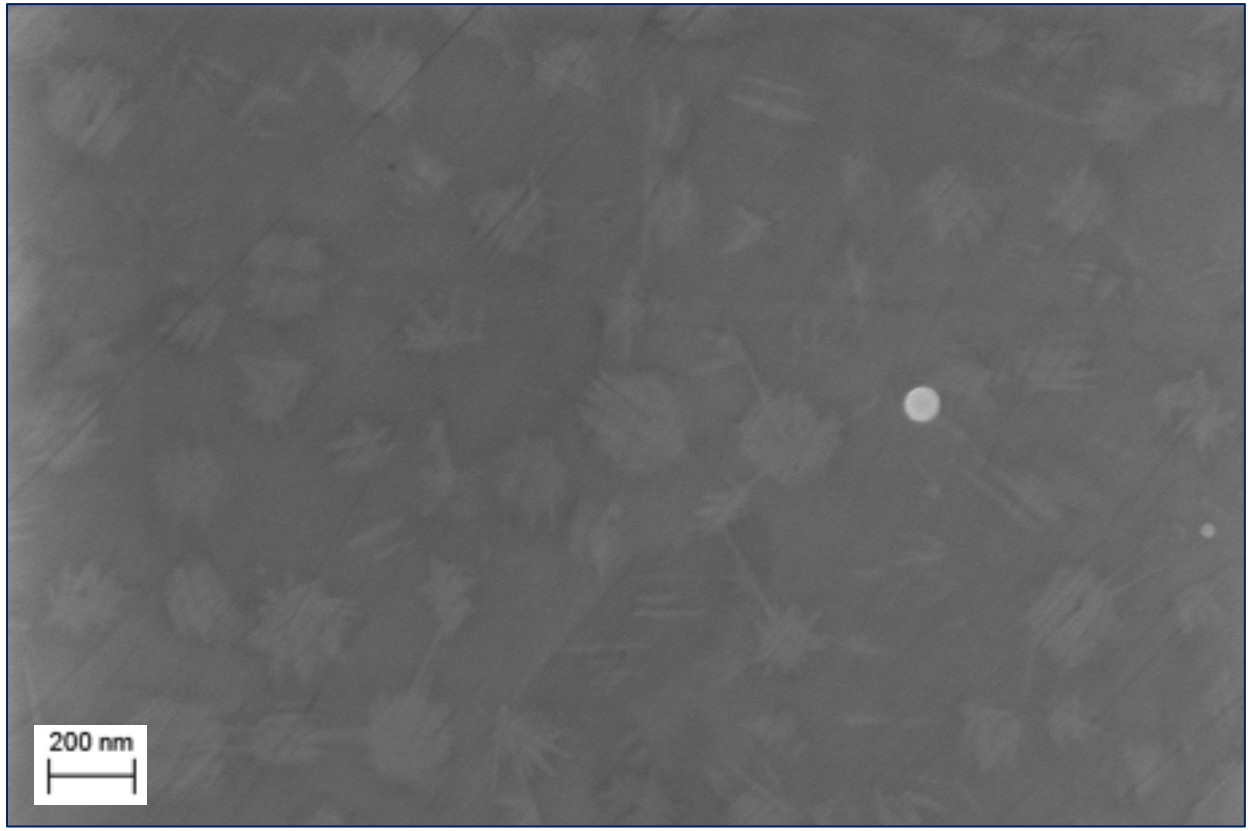
Nucleation Step: Glasses kept at 220 °C for 2 hours followed by growth steps.

Four samples:

1. Base – no heat treatment
2. 30 minute treatment at 250 °C
3. 30 minute treatment at 260 °C
4. 30 minute treatment at 270 °C
    - 60 mins at 270 °C
    - 90 mins at 270 °C

Observance of Crystal Growth

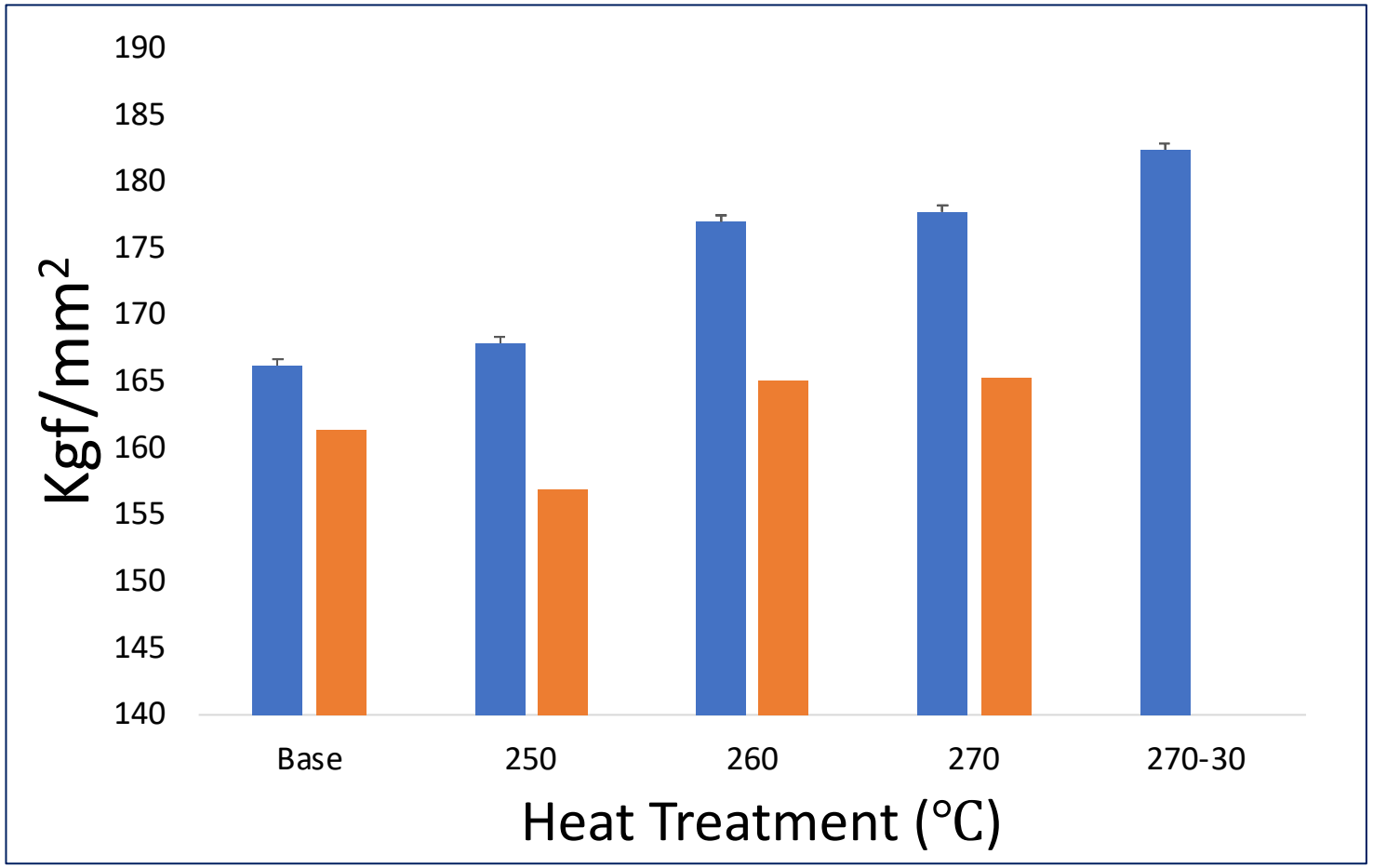
Scanning Electron Microscopy Results



Glass with 60 minutes at 270 °C

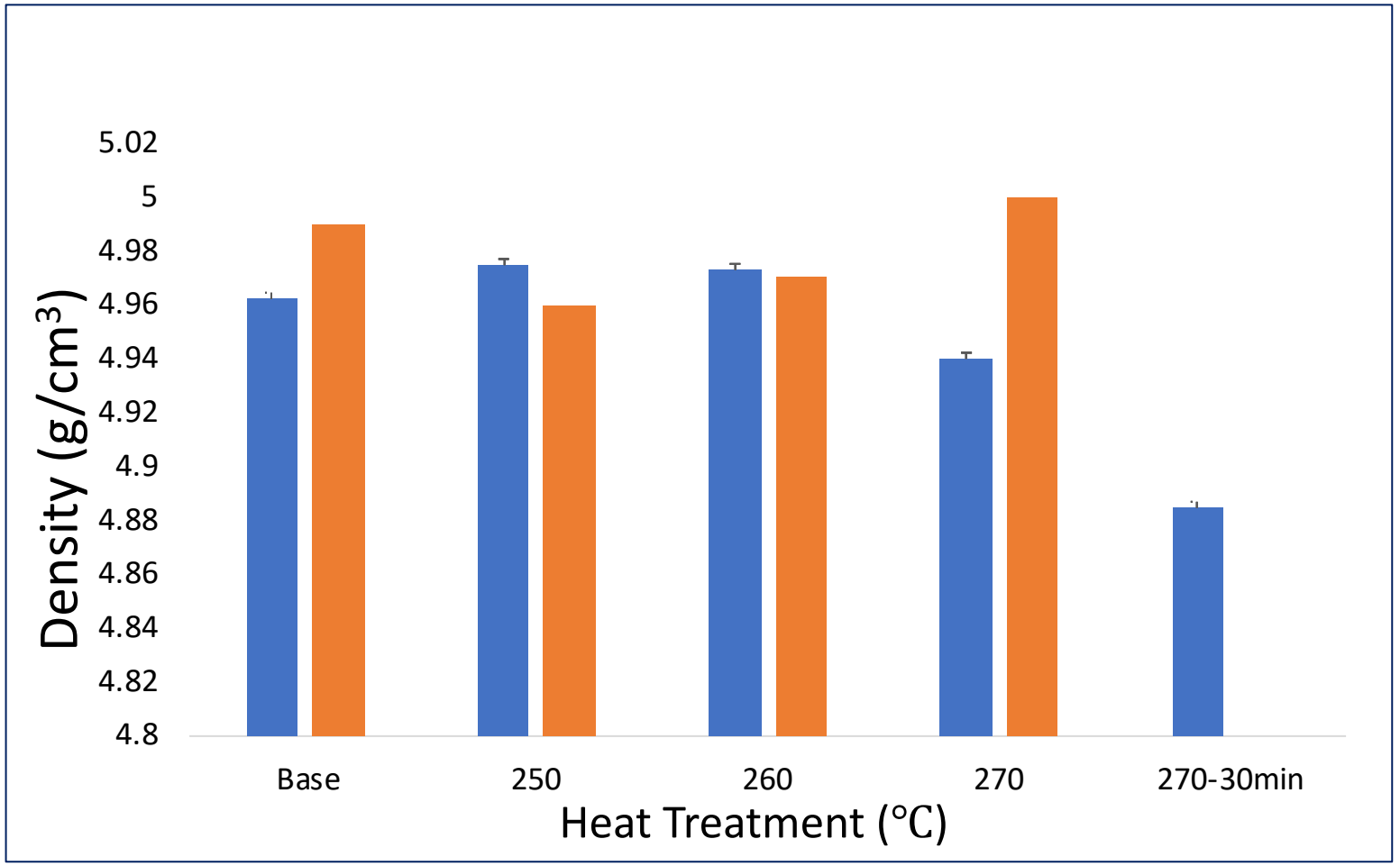
Mechanical Results

Vicker's Hardness Measurements



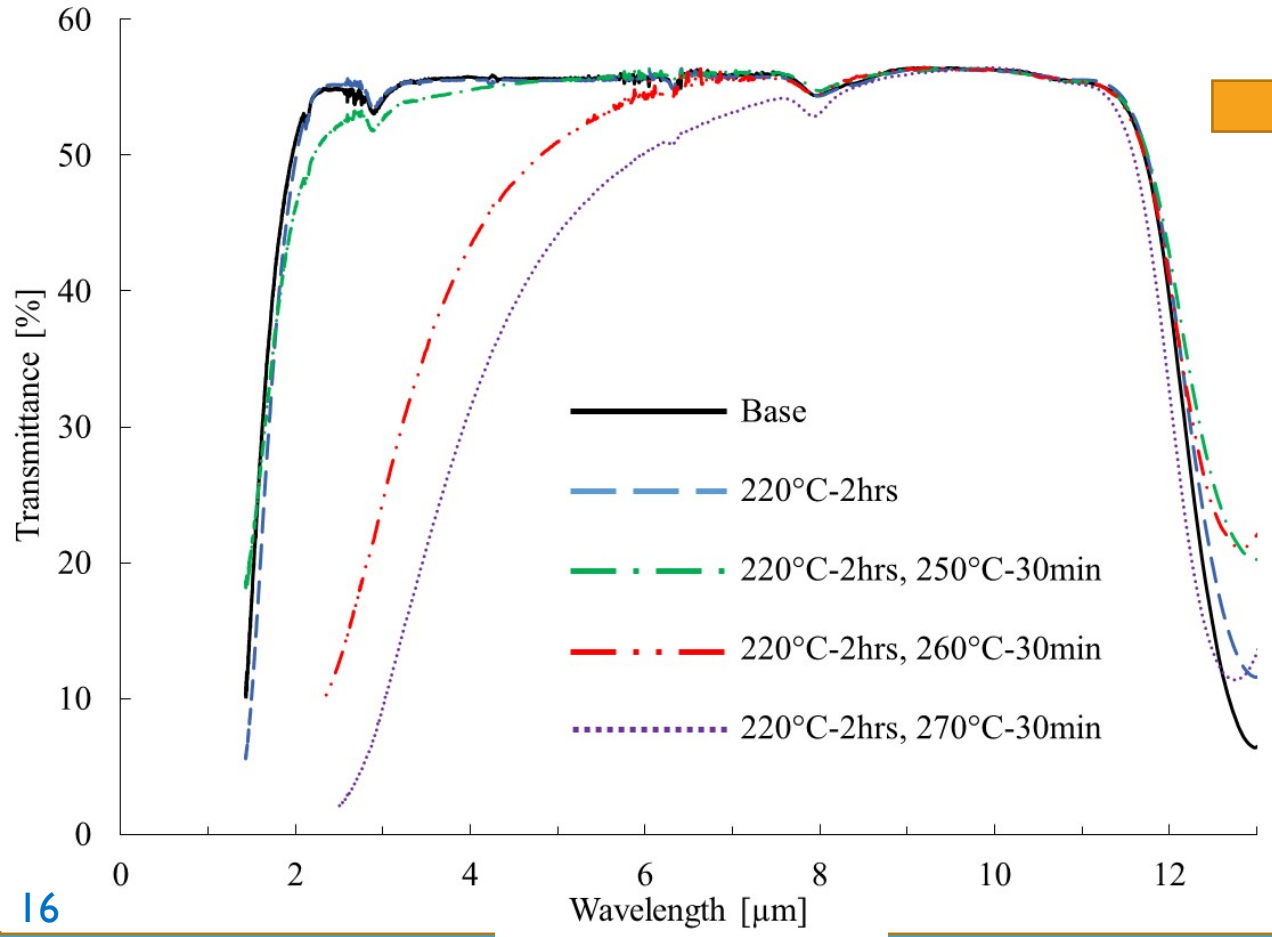
Mechanical Results

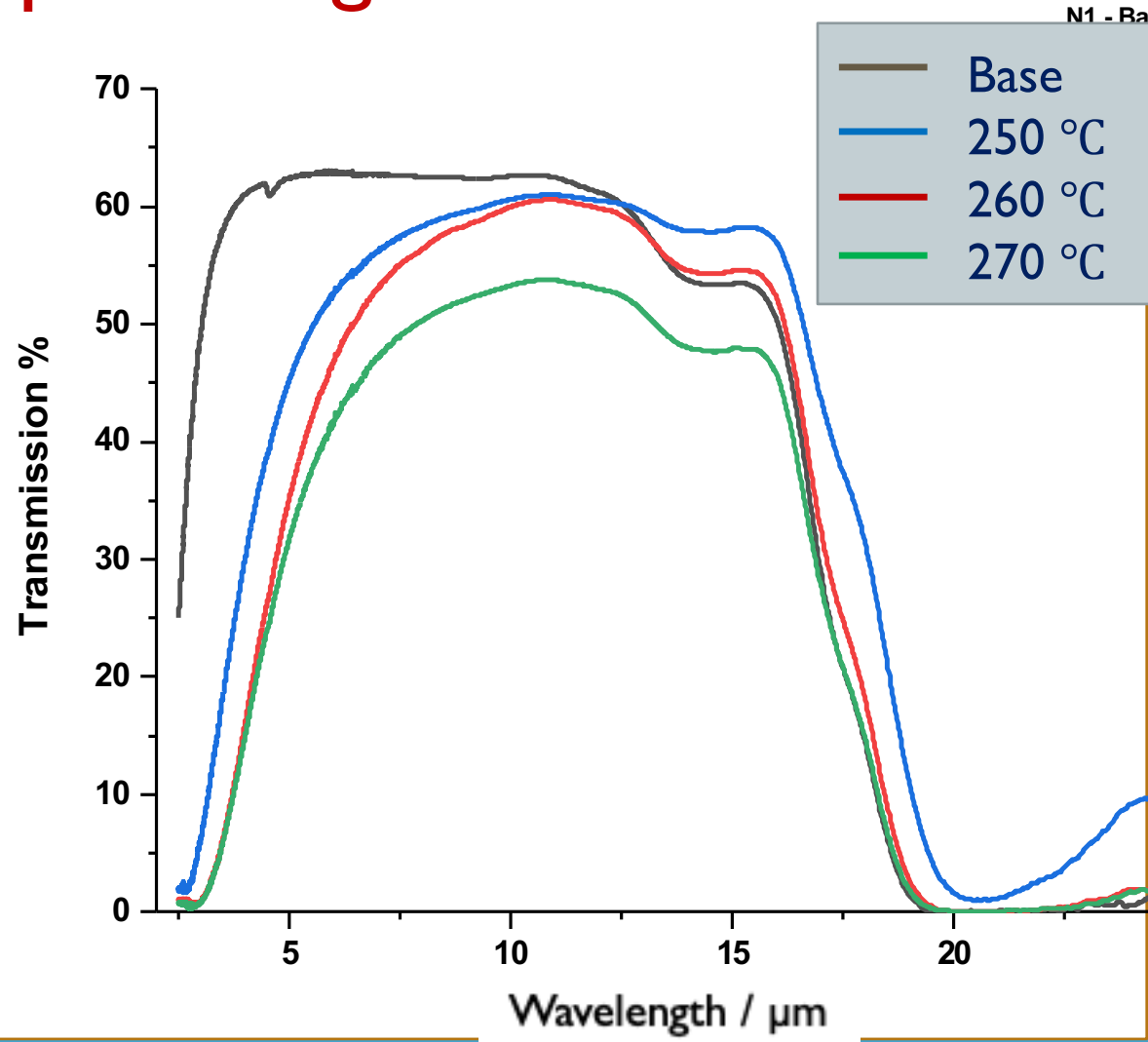
Density Measurements



Transmission Results

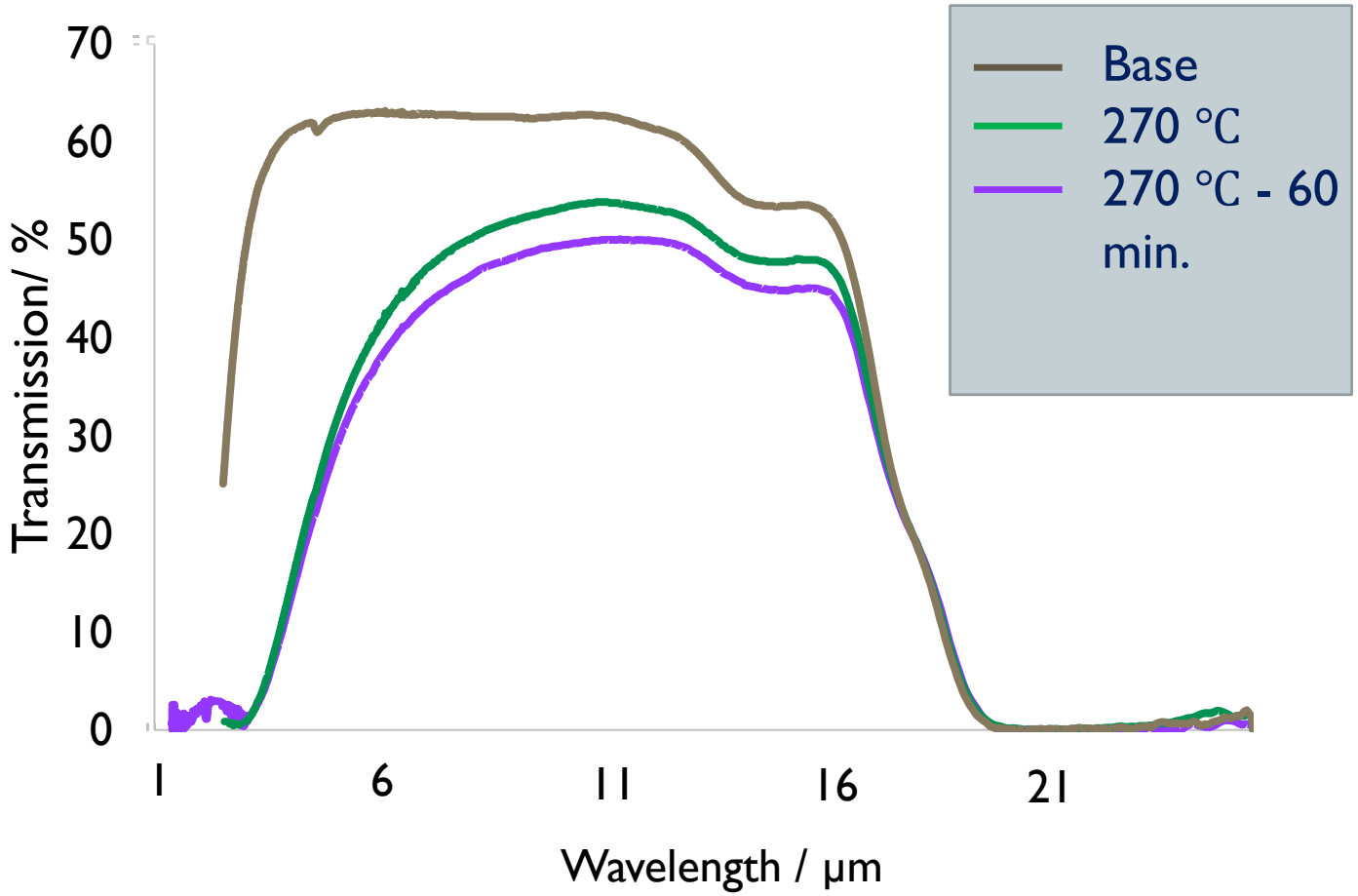
FTIR Measurements of old phase separated glass with new ones





Transmission Results

FTIR Measurements of longer heat treatment time



Conclusions & Future Works

- We were able to use heat treatments to increase the hardness of our
- Longer heat treatments need to be completed to get the maximum hardness values.
- We can use these methods to create more durable chalcogenide glasses.

Works Cited

1. Anupama Yadav, A. B., Myungkoo Kang, Laura Sisken, Charmayne Smith, Jason Lonergan, Cesar Blanco, Michael Antia, Megan Driggers, Andrew Kirk, Clara Rivero-Baleine, Theresa Mayer, Andrew Swisher, Alexej Pogrebnyakov, A. R. Jr. Hilton, Greg Whaley, Thomas J. Loretz, Anthony Yee, Greg Schmidt, Duncan T. Moore, Kathleen A. Richardson, Melt property variation in GeSe2-As2Se3-PbSe glass cermaics for infrared gradient refractive index (GRIN) applications. *Int. J. Appl. Glass Sci.* **2018,** *10*, 27-40.
2. Anupama Yadav, M. K., Charmayne Smith, Jason Lonergan, Andrew Buff, Laura Sisken, Karima Chamma, Cesar Blanco, Joe Caraccio, Theresa Mayer, Clara Rivero-Baleine, Kathleen Richardson, Influence of phase separation on structure-property relationships in the (GeSe2-3As2Se3)1-xPbSex glass system. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B* **2017,** *58* (4), 115-126.
3. Benn Gleason, K. R., Laura Sisken, Charmayne Smith, Refractive index and thermo-optic coefficients of Ge-As-Se chalcogenide glasses. *Int. J. Appl. Glass Sci.* **2016,** *7* (3), 374-383.
4. Laura Sisken, C. S., Andrew Buff, Myungkoo Kang, Karima Chamma, Peter Wachtel, J. David Musgraves, Clara Rivero-Baleine, Andrew Kirk, Matthew Kalinowski, Megan Melvin, Theresa S. Mayer, Kathleen Richardson, Evidence of spatially selective refractive index modification in 15GeSe2-45As2Se3-40PbSe glass ceramic through correlation of structure and optical property measurements for GRIN applications. *Optical Matierals Express* **2017,** *7* (9), 3077-3092.
5. Xia, F. Z., Xianghua; Chen, Guorong; Ma, Hongli; Adam, J. L., Glass formation and crystallization behavior of a novel GeS2-Sb2S3-PbS chalcogenide glass system. *J. Am. Ceram. Soc.* **2006,** *89* (7), 2154-7.
6. Hua Wang, X. Z., Guang Yang, Yinsheng Xu, Hongli Ma, J. L. Adam, Zhen'an Gu, Guorong Chen, Micro-crystallization of the infrared transmitting chalcogenide glass in GeSe2-As2-Se3-PbSe system. *Ceramics International* **2009,** *35*, 83-86.

Thanks!