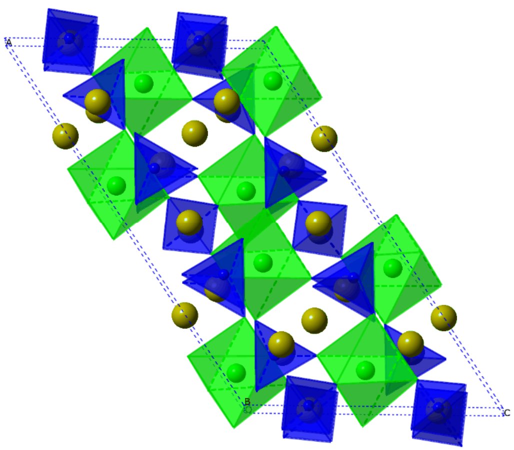
SAND2016-0245C

Sodium-Ion Conductivity and Scaling Effects in NaSICon Thin Films Prepared Via Chemical Solution Deposition



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Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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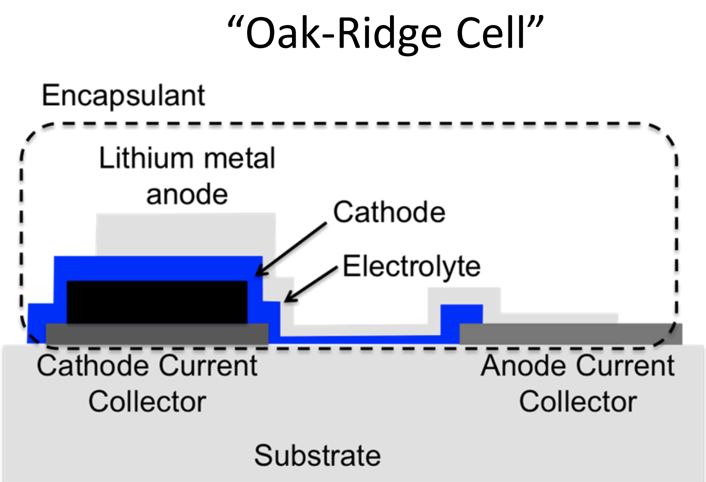
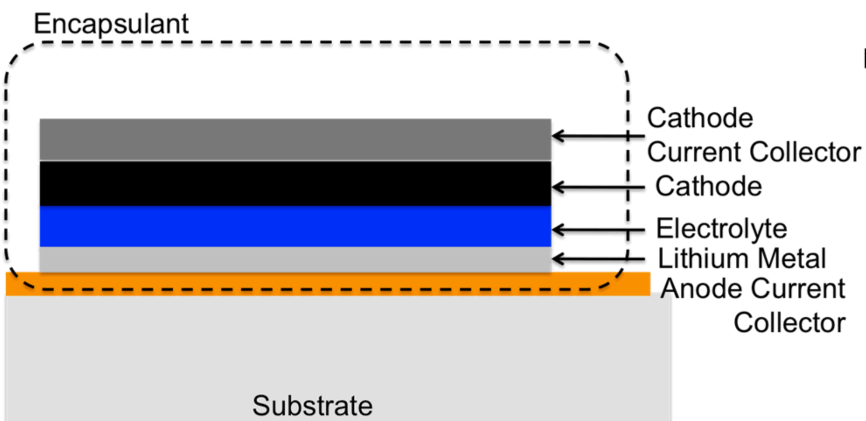
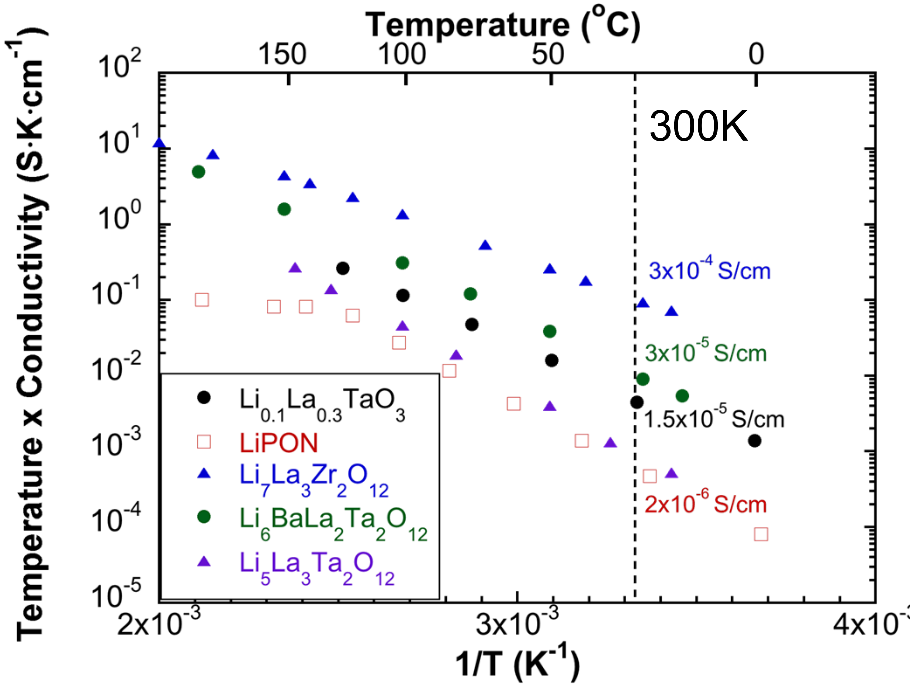
Thin Film Ion Batteries





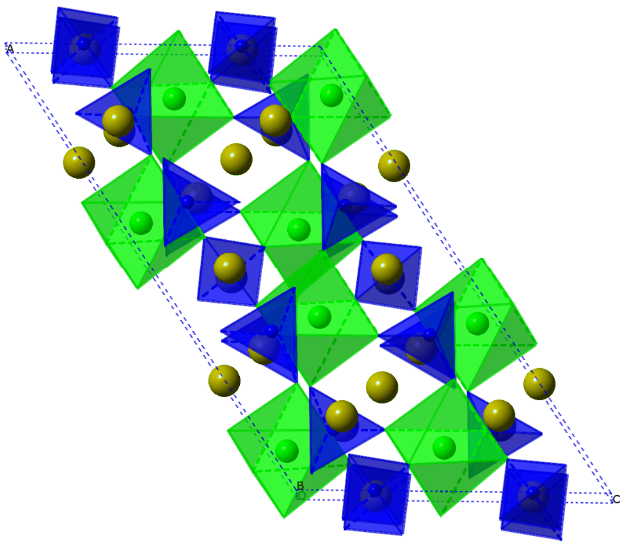


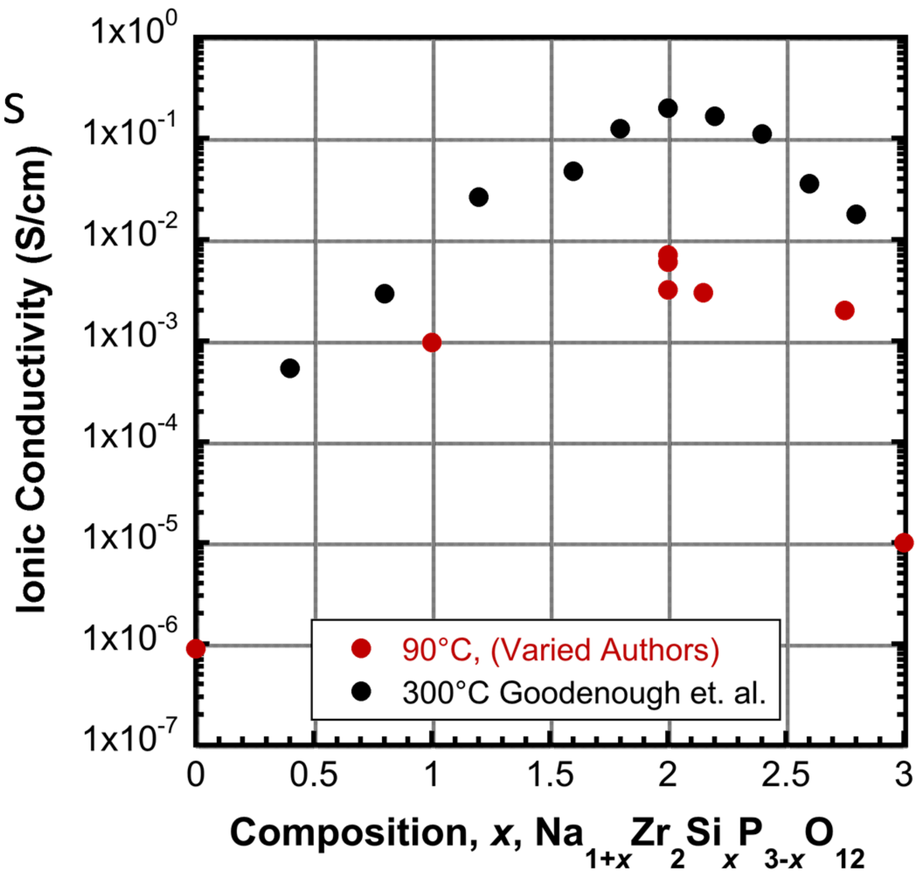
- LiPON is by far the most utilized electrolyte
  - Chemically stable
  - High electrical resistivity
- Ionic conductivity is modest and can limit power output
- ***A higher ionic conductivity electrolyte would be desirable***

Data adapted from: Murugan, *et. al., Angew. Chem. Int. Ed.*, ***46***, *7778 –7781*, (2007), Ihlefeld *et. al. Adv. Mater.*, ***23***, *5663-5667 (2011)*

Sodium Super Ion Conductors "NaSICon"

- $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$
- Extremely high ionic conductivities reported (10^{-3} S/cm) at room temperature
- Limited studies on use in solid-state batteries

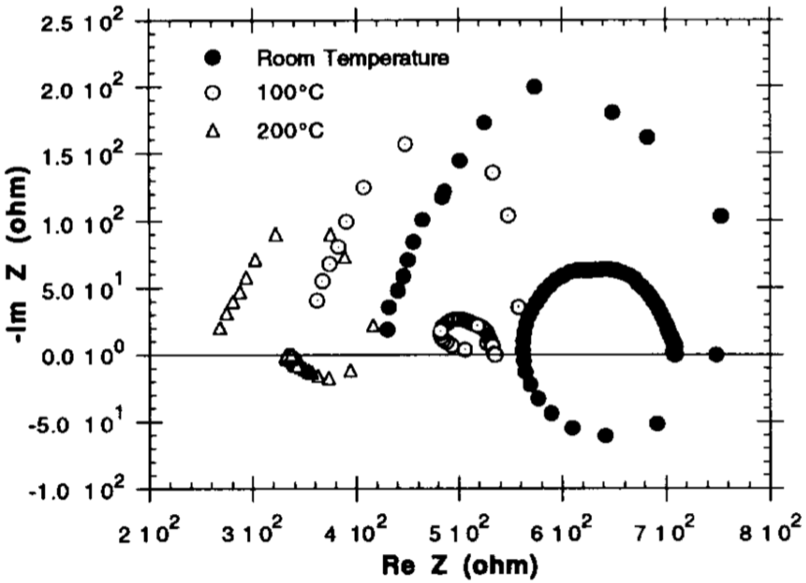




90°C data from Breval, *et. al., Brit. Cer. Trans.*, **93** (76), 239-251 (1994)
300°C data from Goodenough, *et. al., Mater. Res. Bull.*, **11** (2), 203-220 (1976)

NaSICon Thin Film History (It isn't pretty….)

- Extremely limited literature base
- Virtually no rigorous characterization of material properties
- ***Opportunity to make an impact***



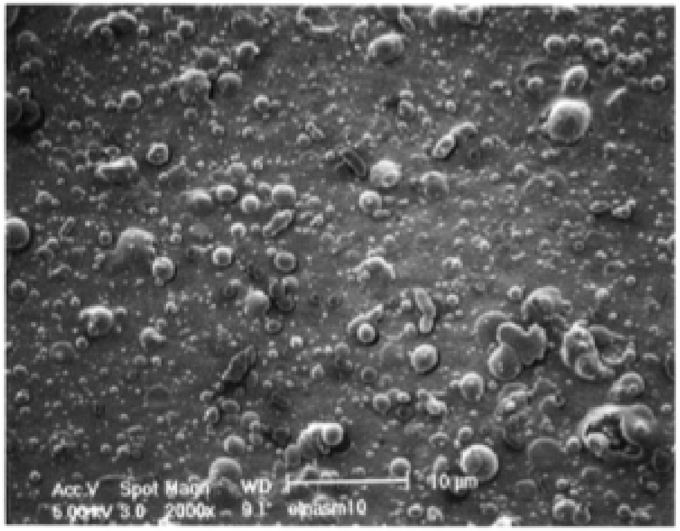


Fig. 2. Micrograph of a NASICON thin film deposited at 1.5 J/cm² on a Raipore membrane.

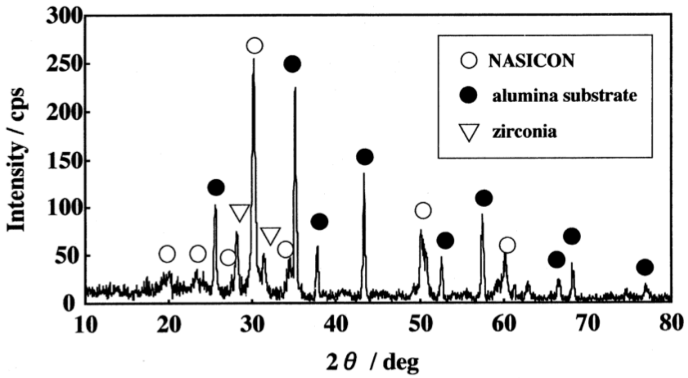


Fig. 7. XRD pattern of the NASICON thin film prepared by spin-coating on an alumina substrate (50 coatings; 1000°C 3 h × 5).

*Citations intentionally omitted

Film Preparation – General Flow

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Zr-Butoxide → 1-Butanol → Dibutylphosphate → 0.15M Solution

TEOS → 0.15M Solution

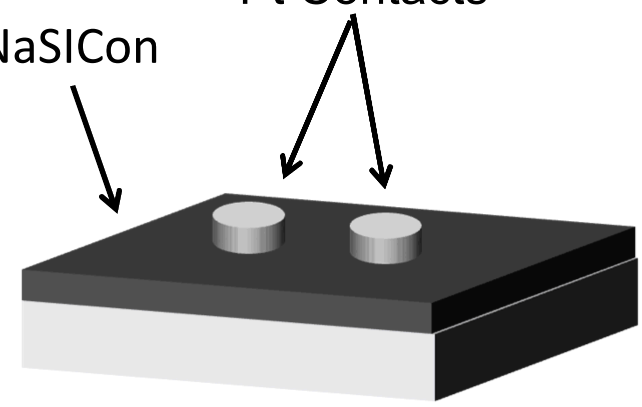
Na-Ethoxide → 0.15M Solution

0.15M Solution → Spin solution on substrate for 30 seconds at 3000 rpm

Spin solution on substrate for 30 seconds at 3000 rpm → Hotplate in air at 300°C for 5 minutes

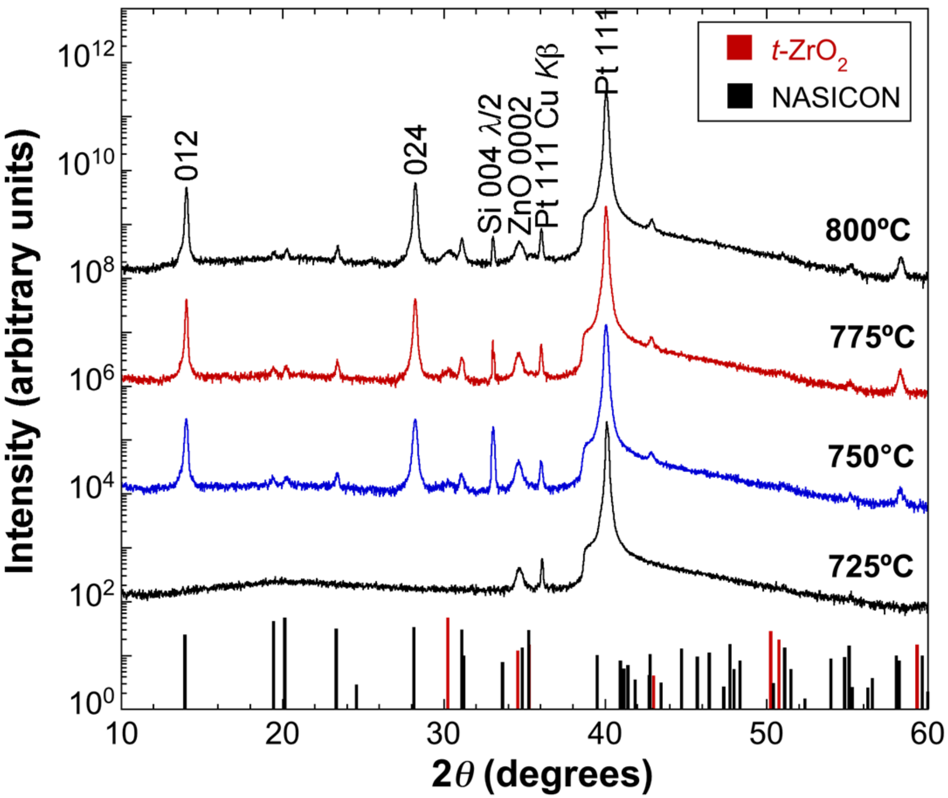
Hotplate in air at 300°C for 5 minutes → Crystallize for 10 minutes at 700°C-800°C in air

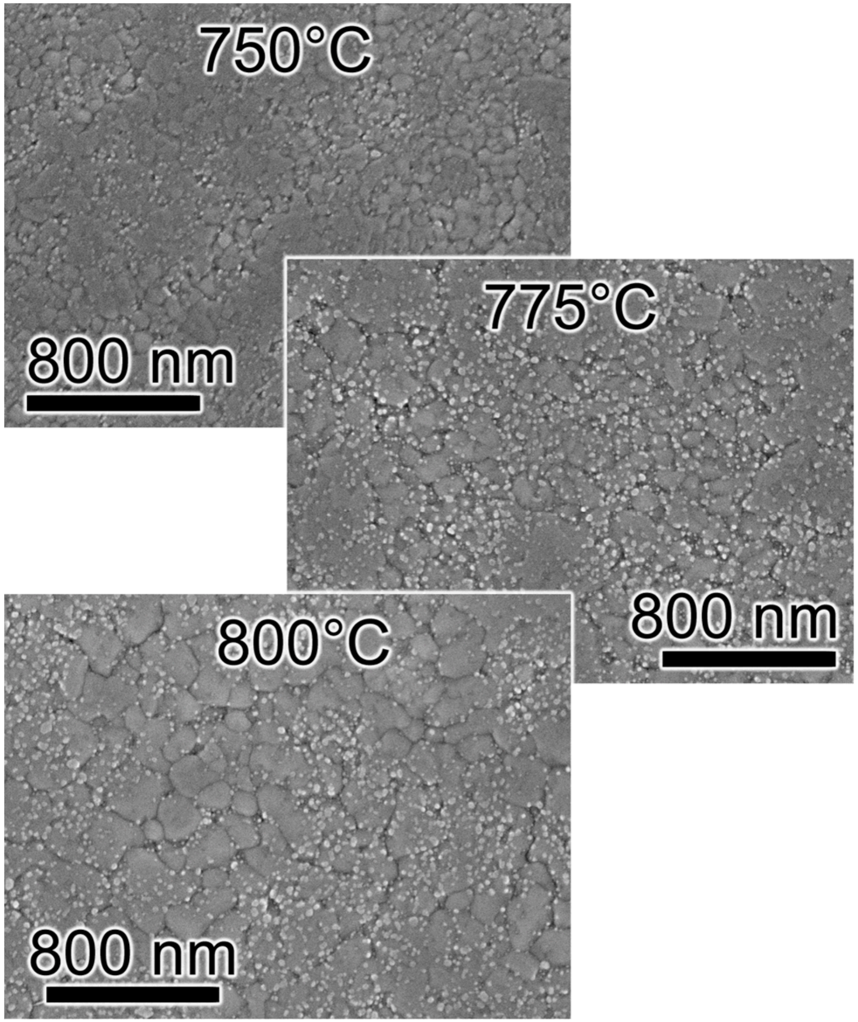
Crystallize for 10 minutes at 700°C-800°C in air → Spin solution on substrate (Repeat for 3 layers)



Solution chemistry loosely based upon:
N. Gasmi, *et al.*, J. Sol-gel Sci. and Tech. **4**, 231-237 (1995) and A. Martucci, *et al.* J. Eur. Cer. Soc., **22**, 1995-2000 (2002)

$NaZr_2P_3O_{12}$ Phase Development and Properties





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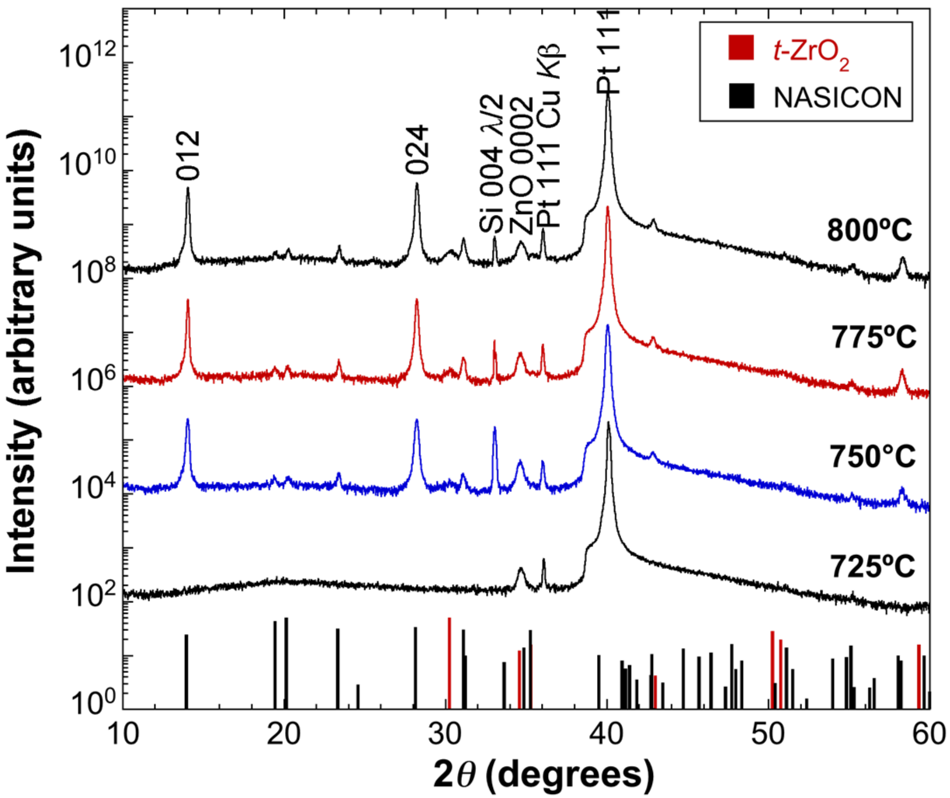
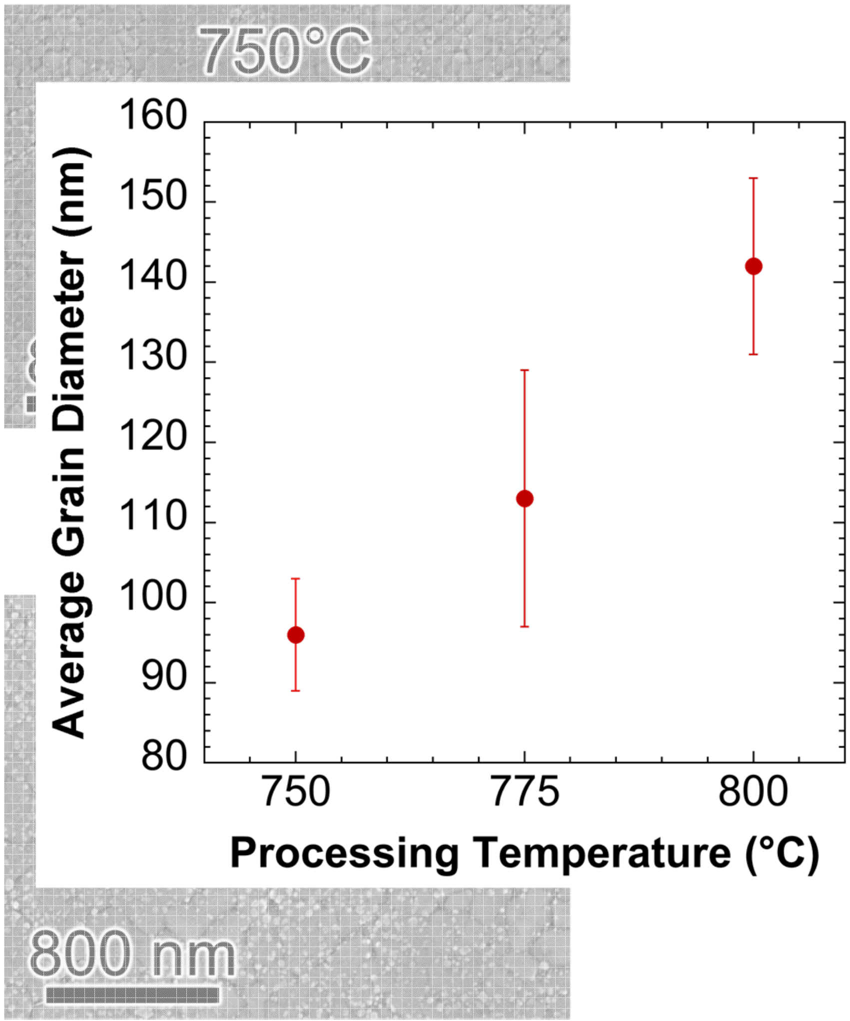
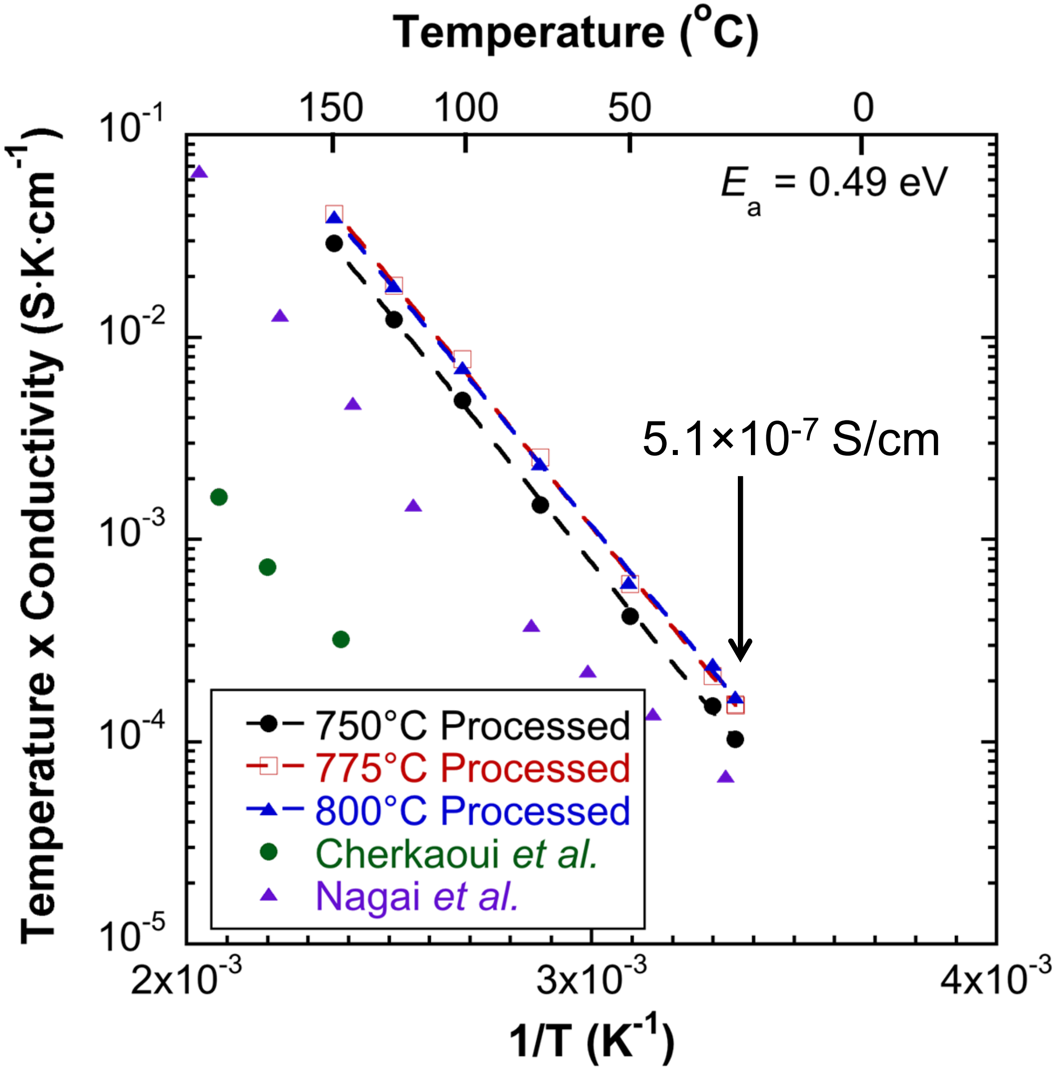




$NaZr_2P_3O_{12}$ Ion-Conductivity Behavior

- Temperature dependence assessed
- Activation Energy of ~0.49 eV calculated
  - Invariant with processing temperature
  - Identical to bulk literature
- Conductivity values compare favorably with bulk ceramics
  - Bulk ceramics noticeably lower conductivity – attributed to lower density (85-90% for Nagai)



Nagai *et. al., J. Amer. Cer. Soc.*, **63** (7-8), 476-477 (1980)
Cherkaoui *et. al., Solid State Ionics*, **21** (4), 333-337 (1986)

W. Meier and J.F. Ihlefeld, *et al., J. Electrochem. Soc.*, **161** (3), A364-A367 (2014)

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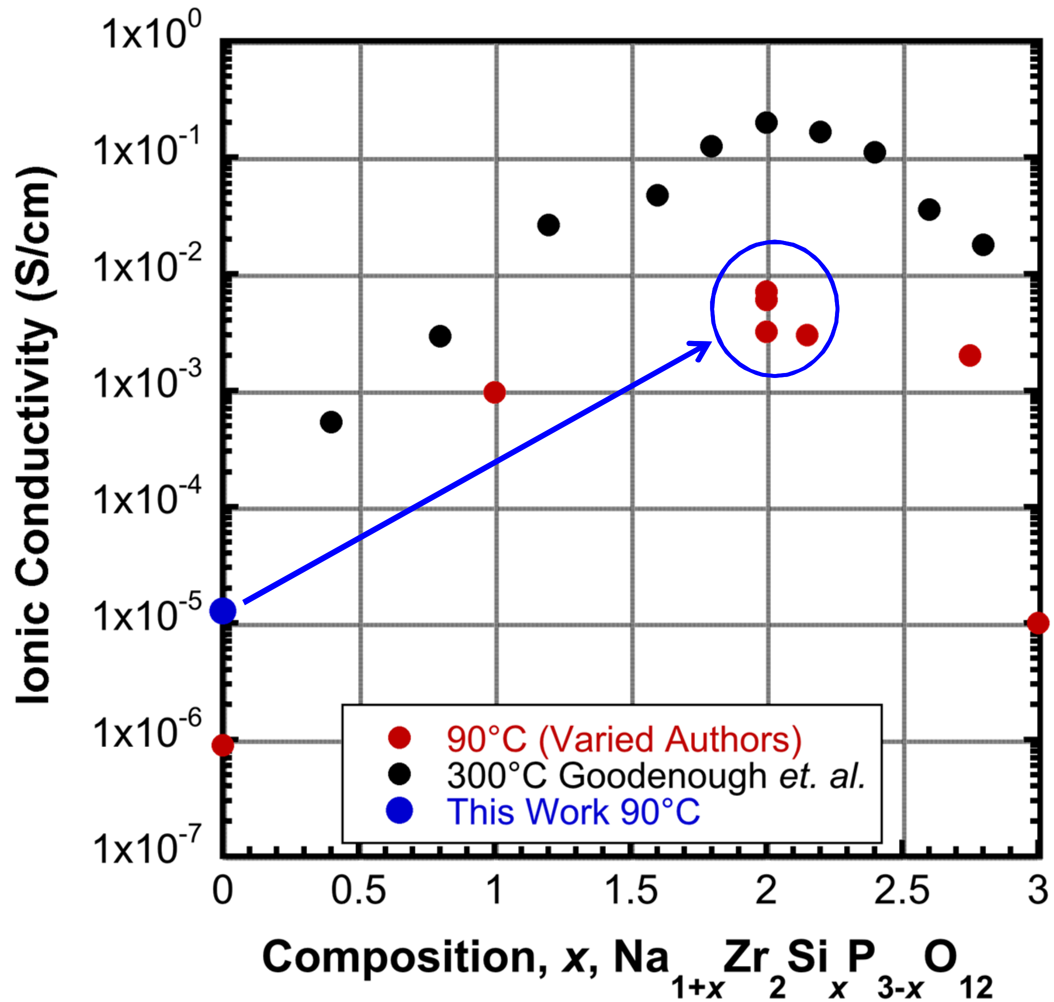

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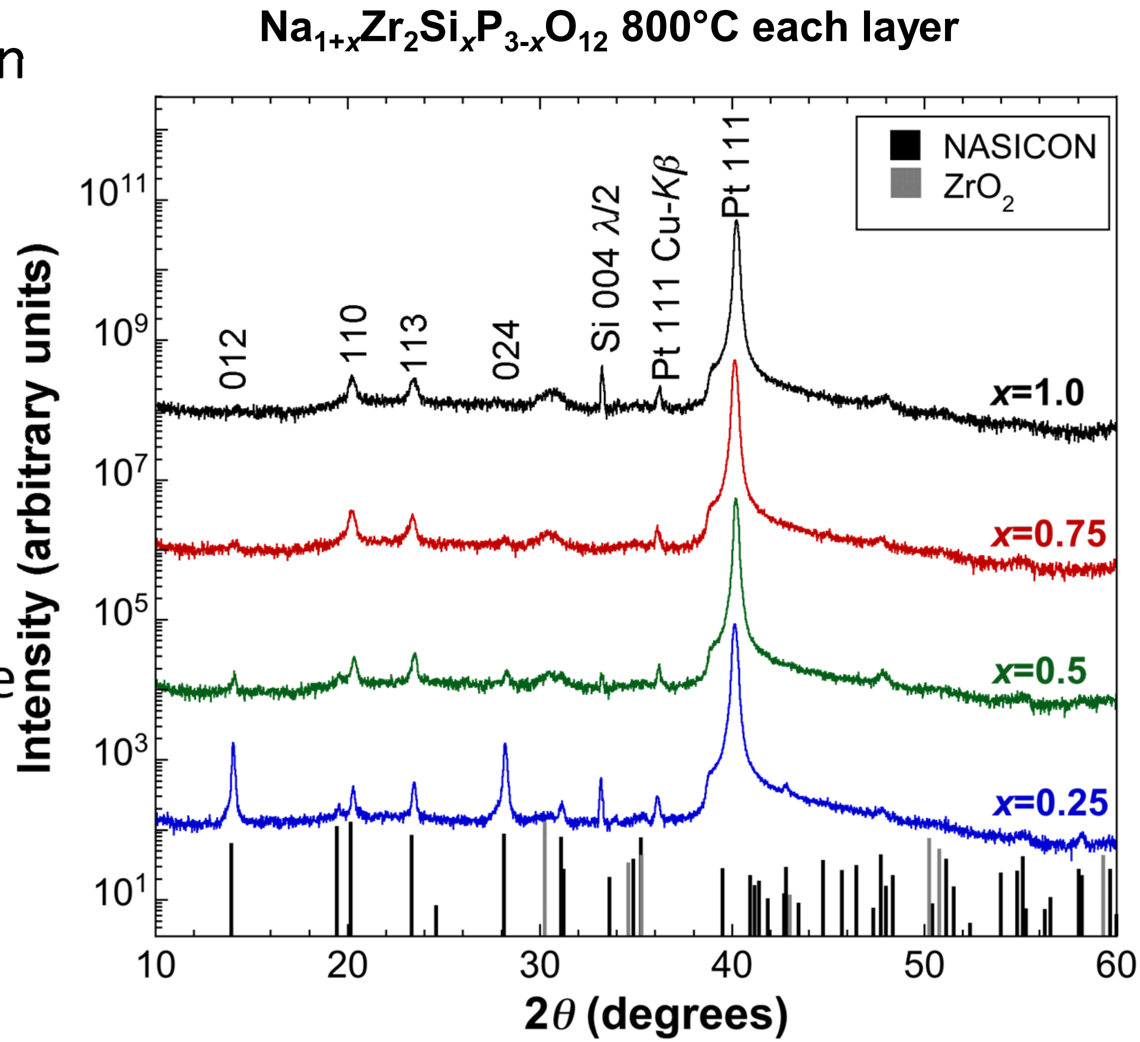
Adding Silicon to the Mix….

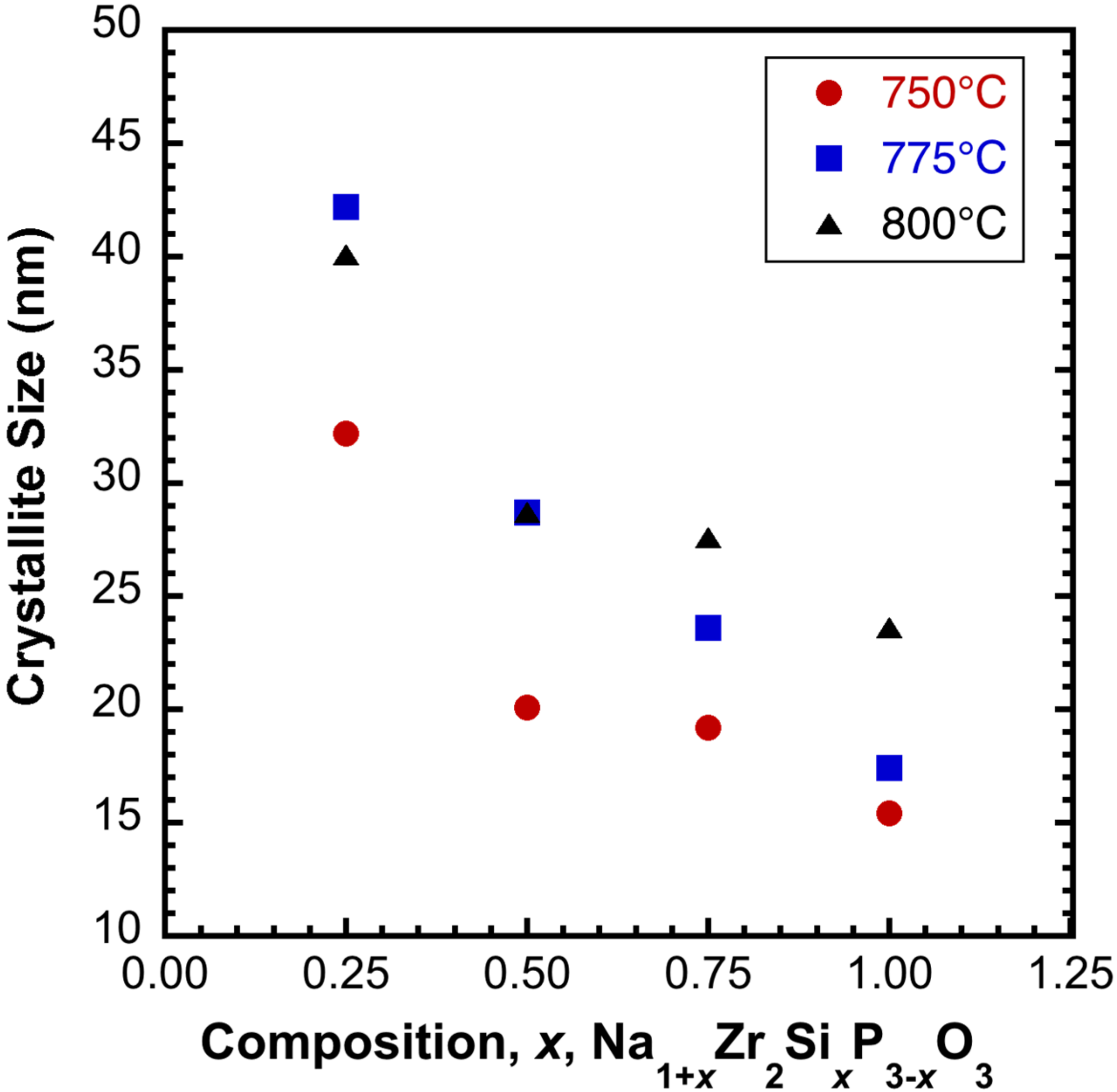
- Preferred texture goes away with increasing silicon content
  - Change in nucleation mechanism?
- X-ray peak widths increase with silicon content
  - Suggests reduced crystallite/grain size
- X-ray peak widths decrease with process temperature
- Possible increase in ZrO_2 peak intensity



J.F. Ihlefeld, *et al., submitted to J. Amer. Ceram. Soc.*

Crystallite size scales with silicon content

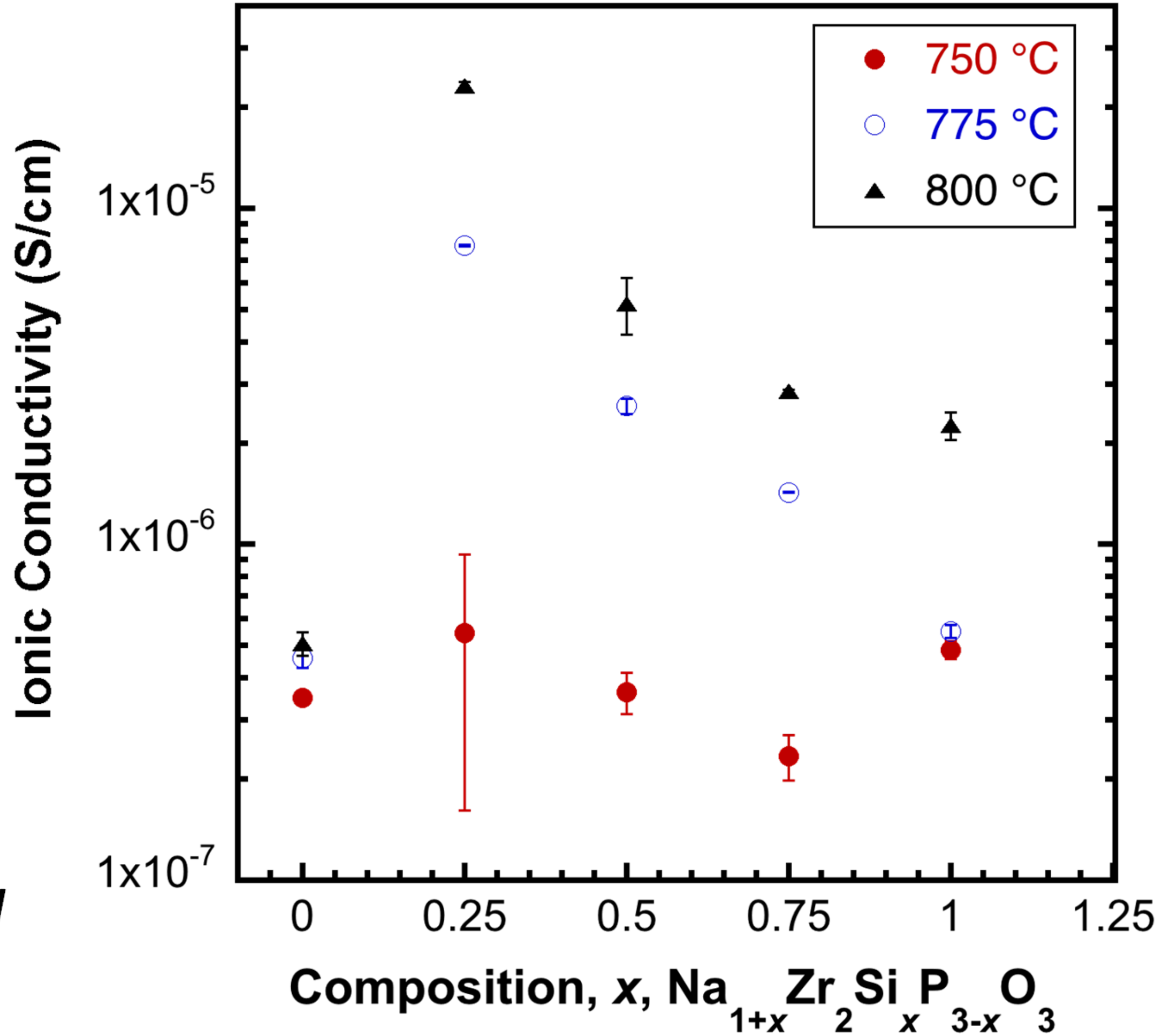
- Crystallite size determined from 110 peak FWHM (Scherrer's Formula)
- Crystallite size decreases with increasing silicon content
  - More refractory?
- Crystallite size decreases with decreasing processing temperature



J.F. Ihlefeld, *et al., submitted to J. Amer. Ceram. Soc.*

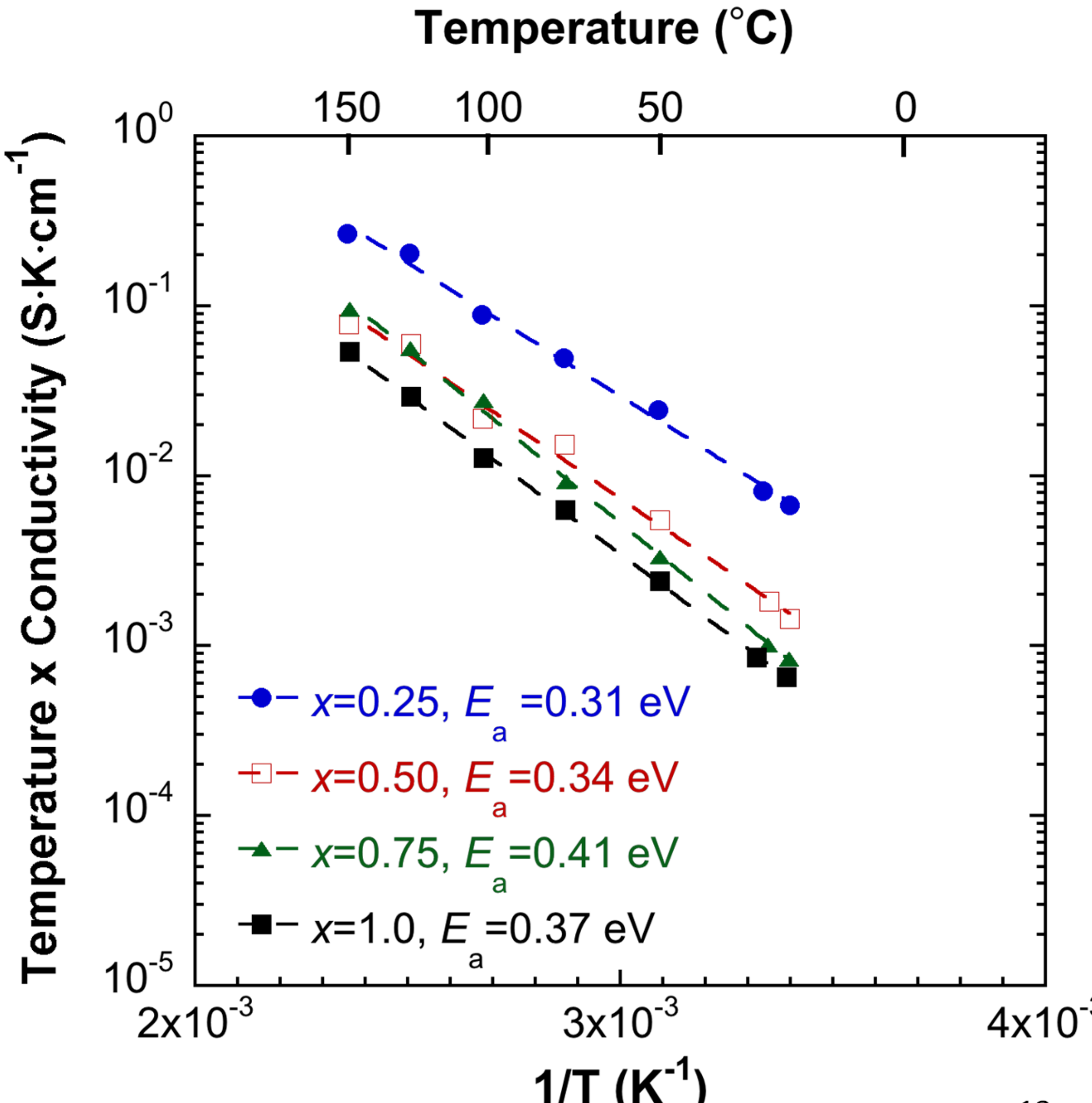
Ionic conductivity scales with silicon content

- Increase in ionic conductivity at x=0.25
- Decrease in ionic conductivity with x>0.25
  - ***Different than expected bulk response***
- Increased ionic conductivity with increase process temperature for each composition
  - ***Consistent with increased crystallite size***



Ionic conductivity scales with silicon content

- Maximum ionic conductivity for *x*=0.25 composition
- Activation energies for ionic conduction consistent with bulk values for same compositions
  - *x*>0.25 films *act* like bulk conductors, but have depressed values
- ***Decreasing crystalline perfection appears to dominate response***



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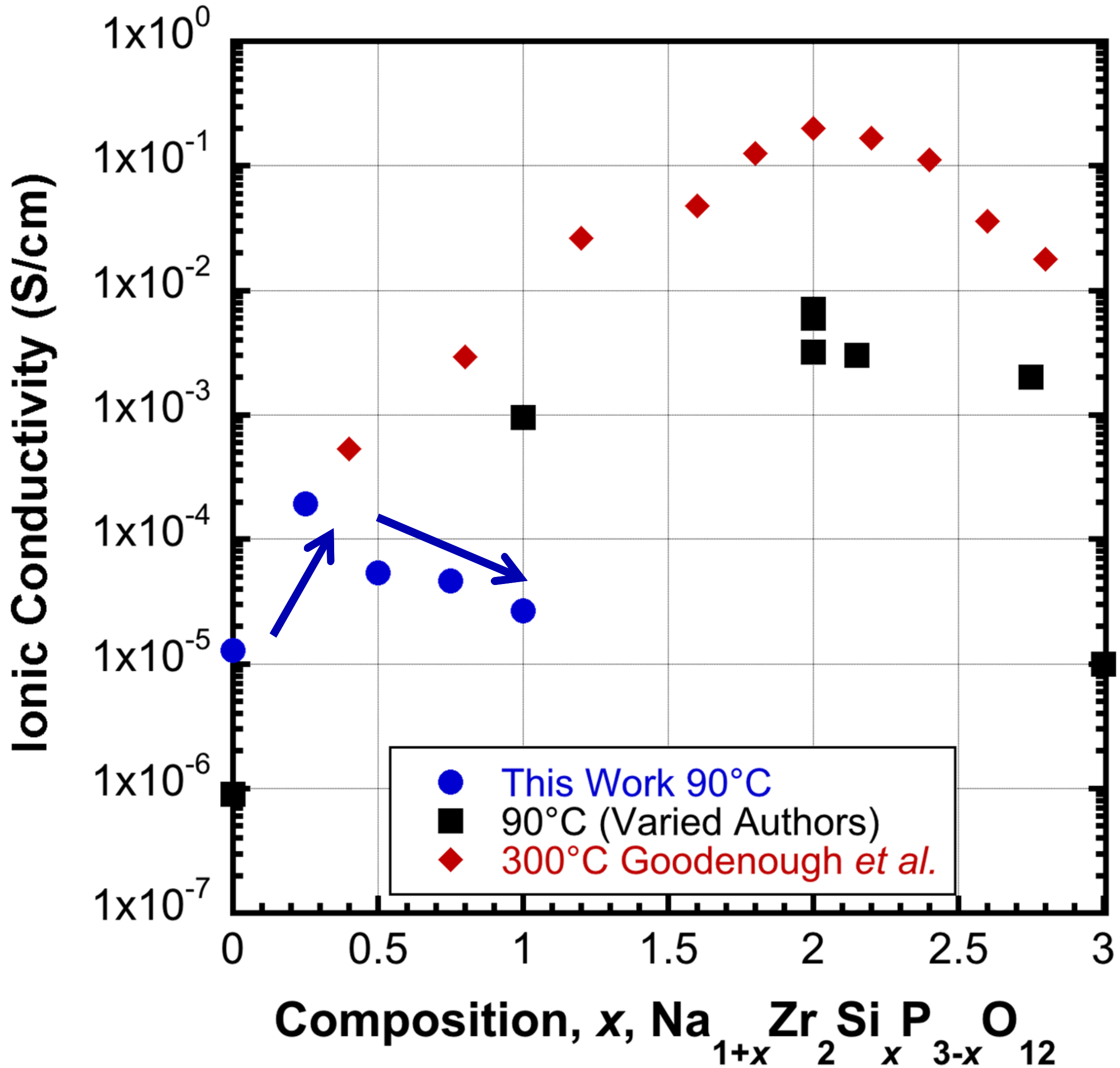
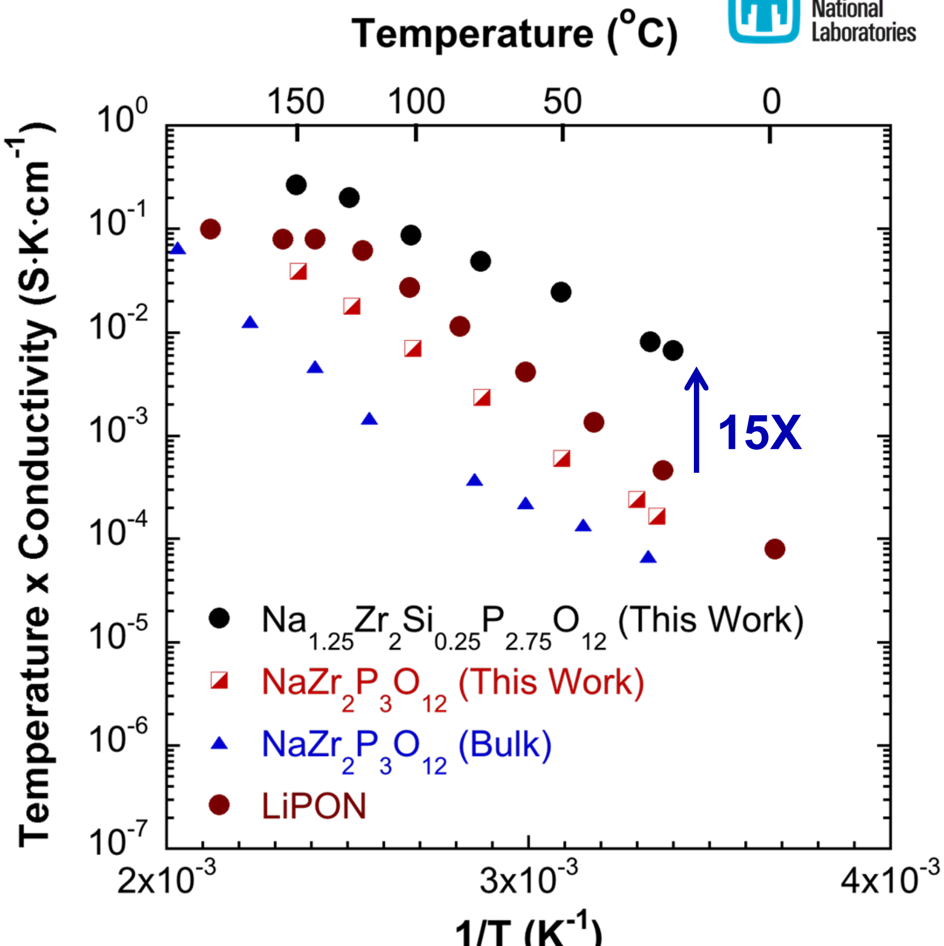


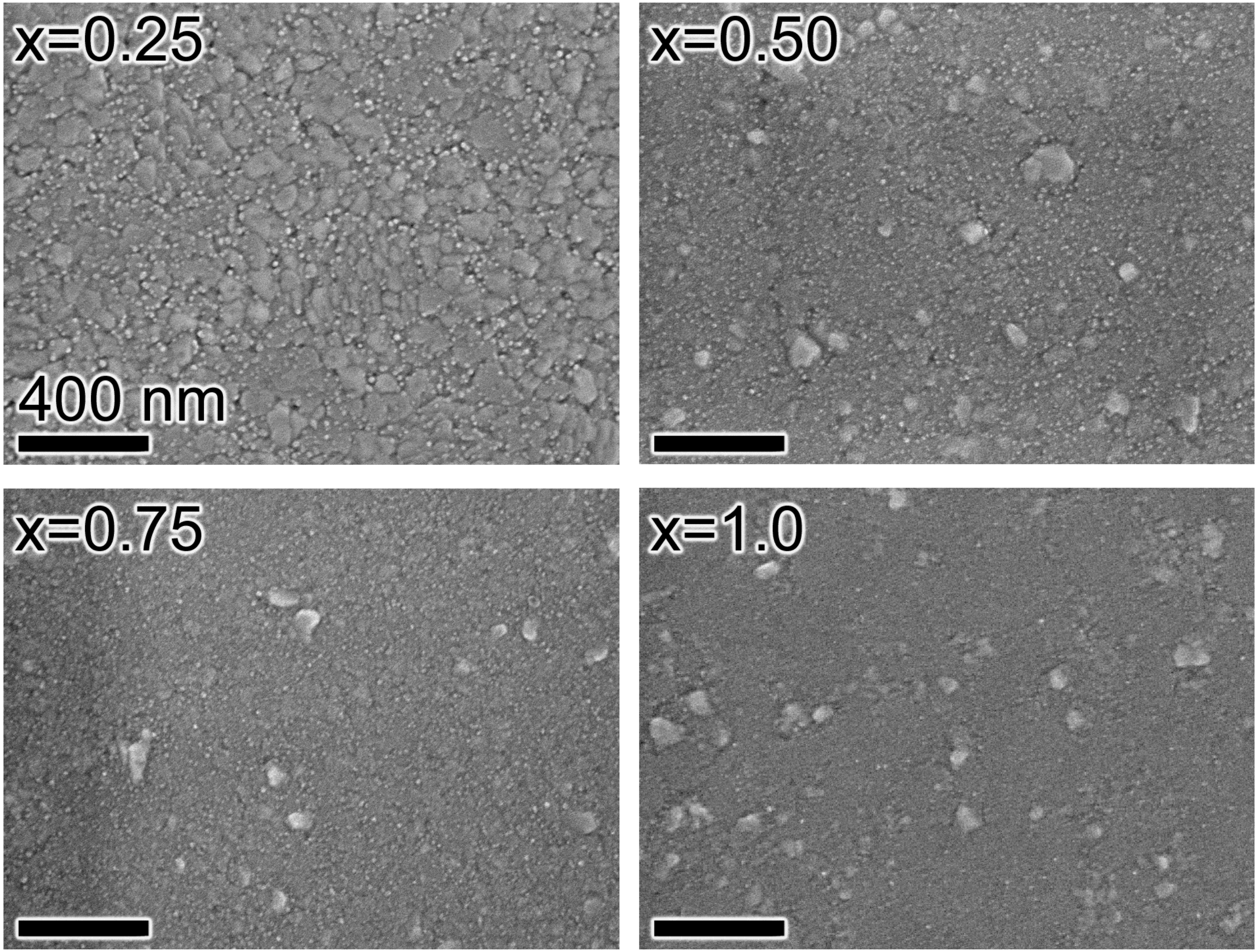
Summary

- NaSICon thin films can be prepared via a simple chemical solution technique (up to *x*=1)
- *NaSICon films can have ion conductivities higher than bulk counterparts*
  - *Likely due to improved density*
- Addition of silicon to *x*=0.25 results in an 60 × conductivity increase
- Additional silicon substitution results in decreased conductivity
  - Poor crystallinity
  - Fine grain size



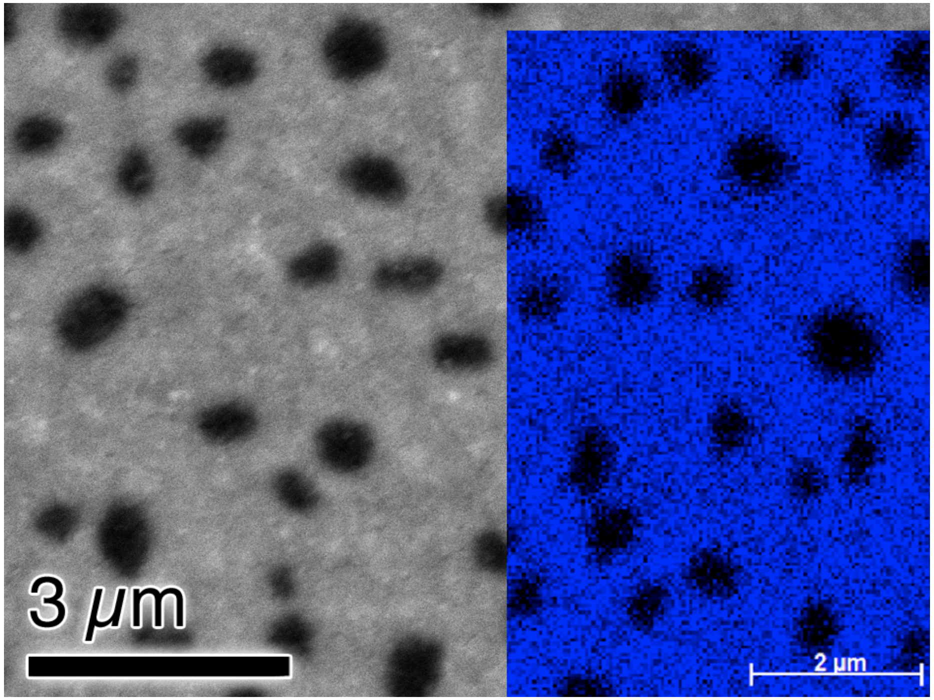
- ***Solid state Na-ion batteries are a promising alternative to lithium particularly for high power applications***

Microstructure Changes with Composition



Why not go hotter? *Electrode Instability*

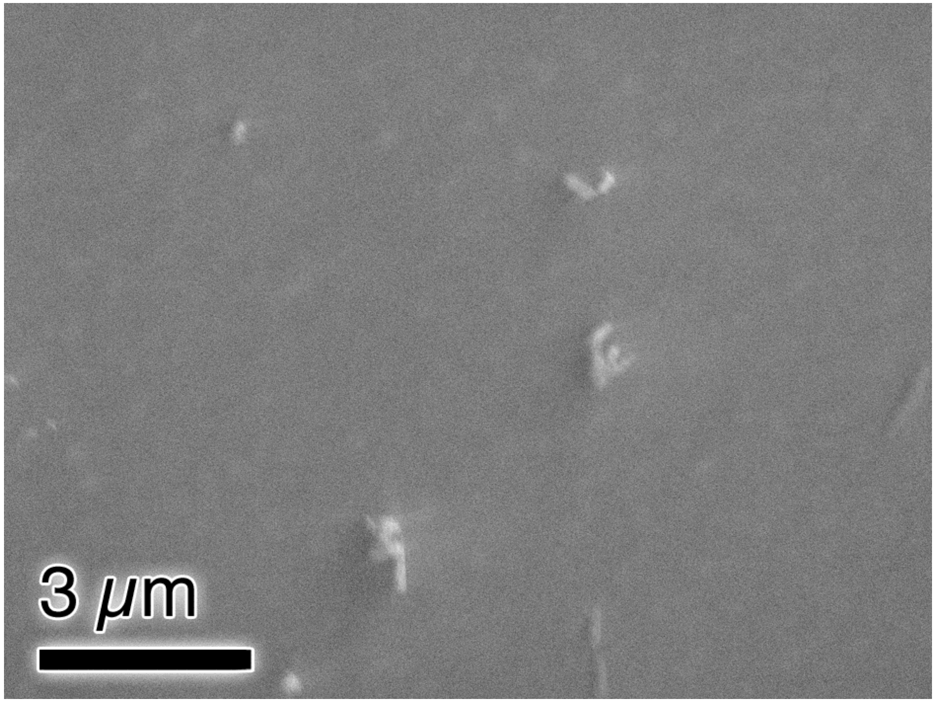
x=1 NaSICon on Pt/ZnO/SiO_2/Si after 800°C



SE2 at 15 kV — Pt EDS Map

Holes in the Pt Layer
(Reaction with Na)

x=1 NaSICon on Pt/TiO_x/SiO_2/Si after 800°C

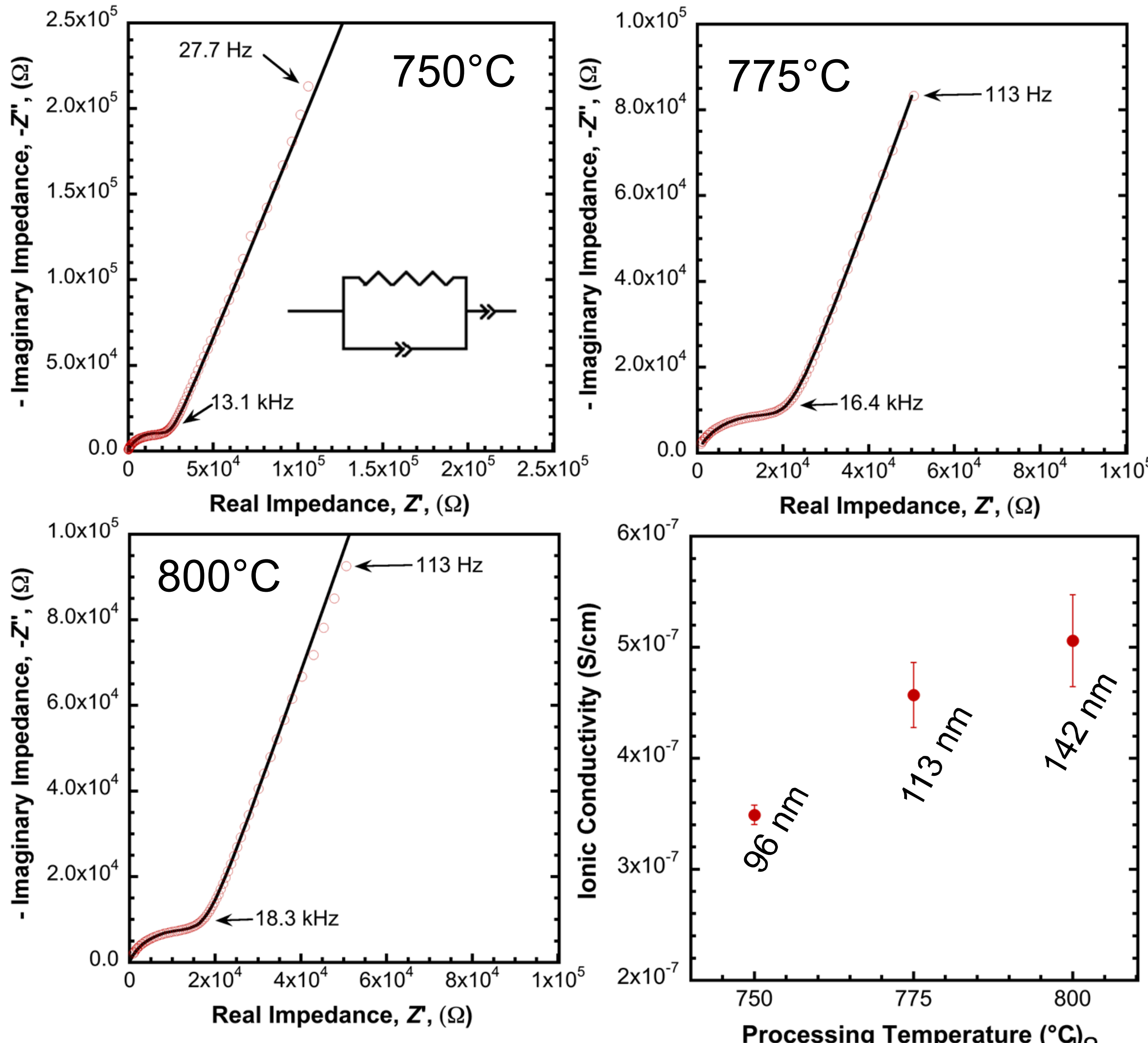


SE2 at 20 kV

No Holes in the Pt Layer
(Interdiffused Ti May Pin Pt)

$NaZr_2P_3O_{12}$ Impedance Response

- Pt/NZP/Pt structures prepared
- Ion-blocking behavior confirmed for each film
- Ion conductivities calculated from resistive element
- Clear trend of increasing conductivity with grain size



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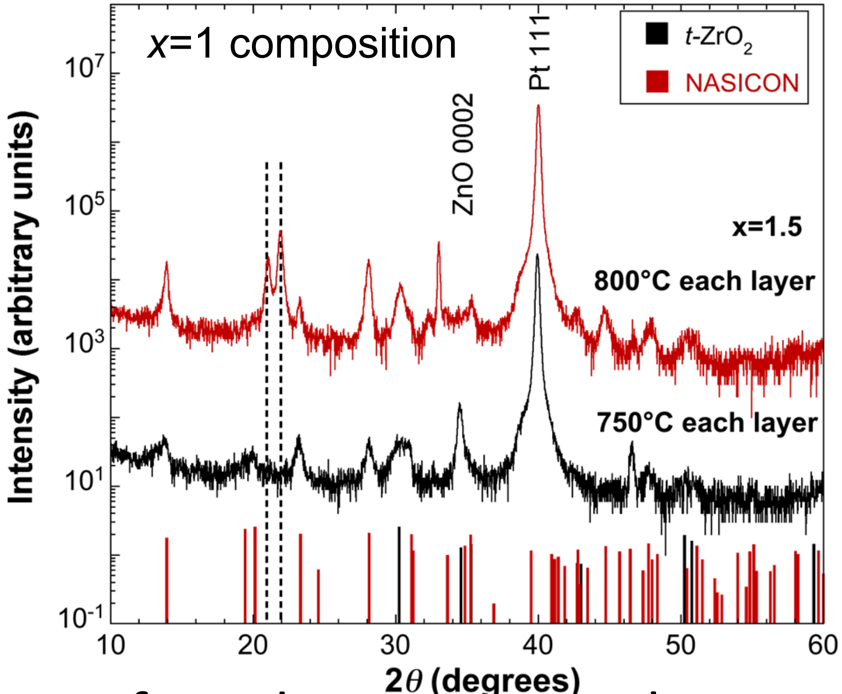
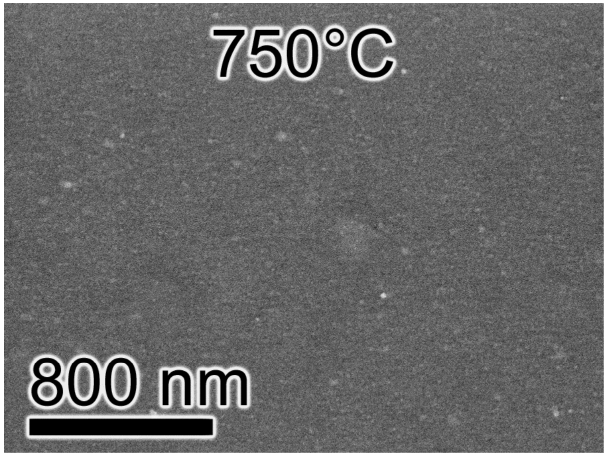
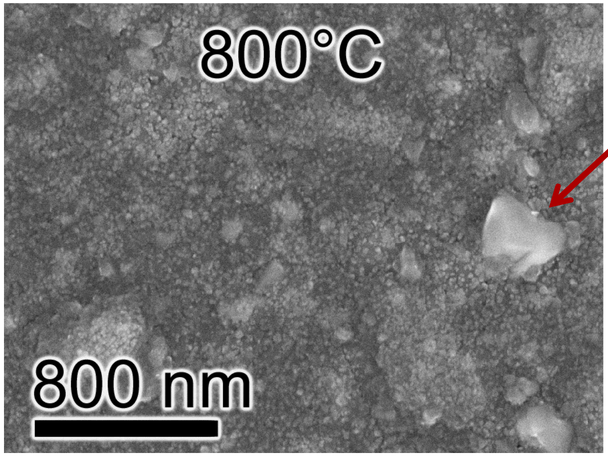


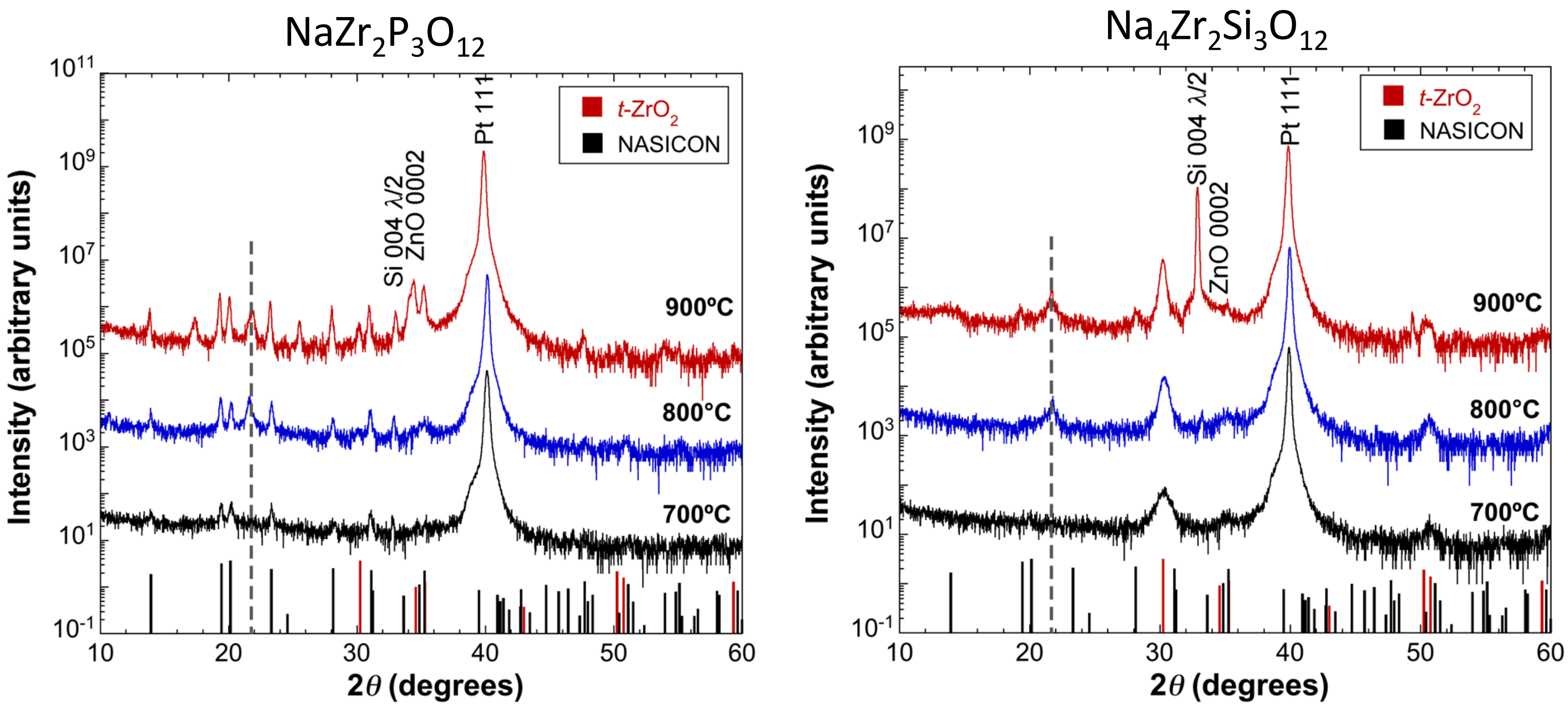
- Preferred texture not observed
- ZrO_2 secondary phase becomes more prominent
- Grain size drastically reduced
- *Heating to higher temperatures results in secondary phase*





Secondary phase

Phase Development: Initial Observations



- Every layer fired to 700° C x 10 minutes, 30 minute post anneal at designated temperatures
- Can unambiguously identify NaSICon peaks in NZP films
- Silicon end-member is comprised of ZrO_2 and an unknown phase

Rigorous Study of $NaZr_2P_3O_{12}$ Phase Development and Properties