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National Nuclear Security Administration

"Phased and Confused": Exploring the Evolution of Phase Chemistry in Sol-gel NaSICON Synthesis

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S1: Functional and Multifunctional Electroceramics for Commercialization
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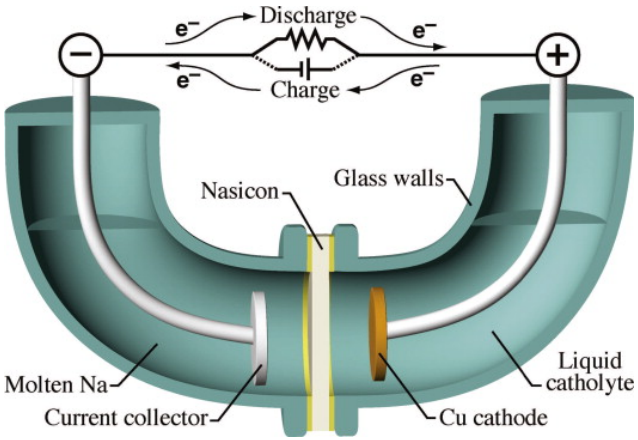
Sodium-based Batteries

Program Focus: Develop sodium-based battery chemistries for large scale energy storage

- Sodium-air
- Sodium-ion
- Low temperature sodium-sulfur
- Sodium-bromine: $Na + \frac{1}{2} Br_2 \leftrightarrows Na^+ + Br^-$
- Sodium-iodine: $Na + \frac{1}{2} I_2 \leftrightarrows Na^+ + I^-$
- Sodium-copper iodide: $Na + CuI_2^- \leftrightarrows Na^+ + 2I^- + Cu(s)$

$$Na \xrightarrow{discharge} Na^+ + e^-$$

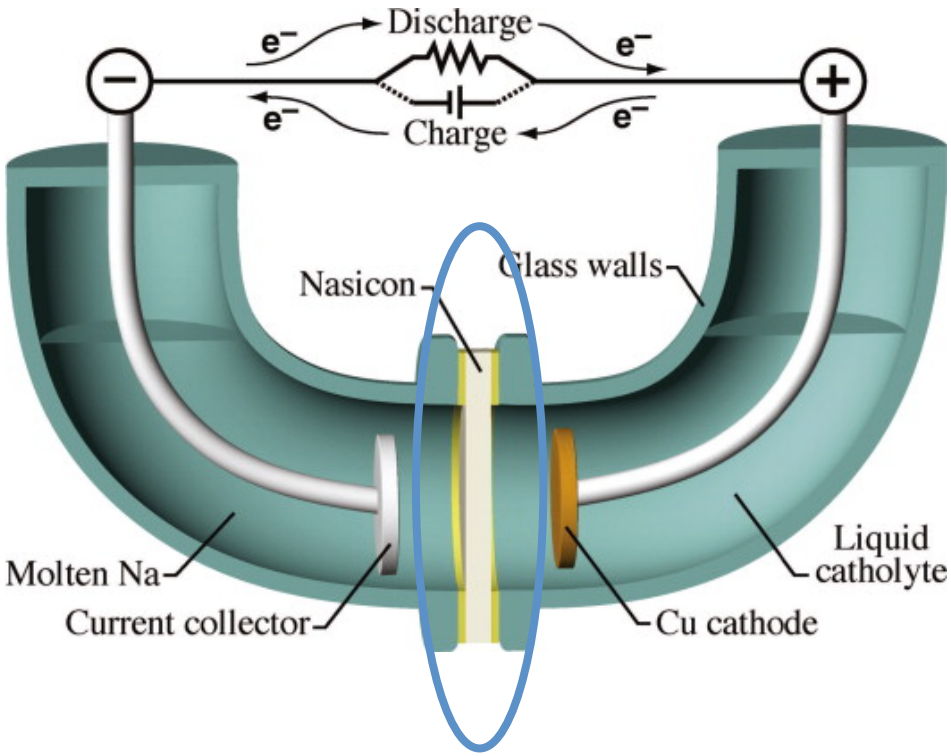


$$CuI_2^- + e^- \xrightarrow{discharge} Cu(s) + 2I^-$$

H. Zhu, S. Bhavaraju, and R. Kee. "Computational model of a sodium–copper-iodide rechargeable battery," Electrochimica Acta (2013).

Na-Based Batteries Depend on Ceramic Solid State Electrolytes

The ceramic separator is central to Na-battery performance!



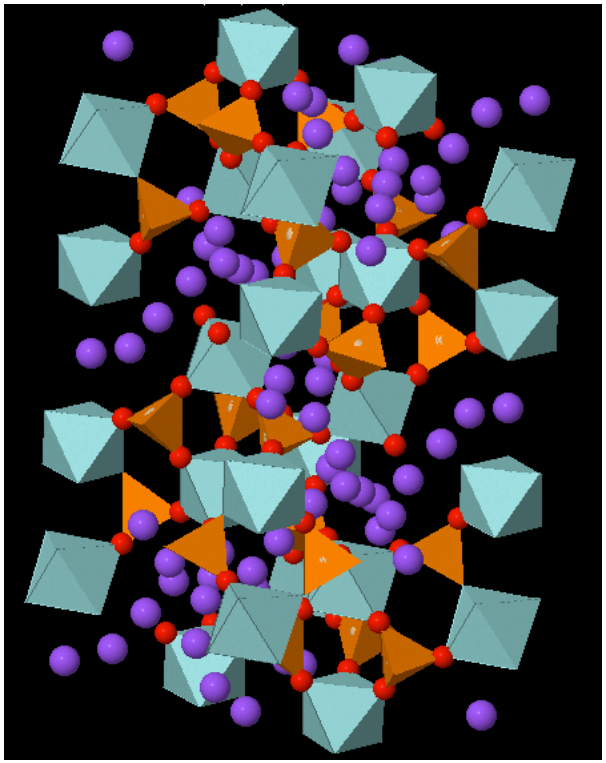
Ceramic requirements:

- High ionic conductivity
- High electrical resistivity
- Robust stability in extreme chemical environments
- Facile, low cost synthesis

NaSICON Ceramic Electrolytes

What is NaSICON? (Sodium (**Na**) **S**uper **I**onic **Con**ductor)

$$Na_{1+x}Zr_2P_{3-x}Si_xO_{12} \xrightarrow{x = 2} Na_3Zr_2PSi_2O_{12}$$



Key NaSICON attributes:

- High ionic conductivity (up to 10^{-2} S/cm at RT) ?
- High electrical resistivity
- Robust stability in extreme chemical environments ?
- Facile, low cost synthesis ?

These qualities all depend on the materials chemistry of the ceramic!

Research Focus: NaSICON Ceramic Solid State Electrolytes

- Understanding the materials chemistry of the solid-state ion-conductor NaSICON
- Correlating material chemistry to materials properties (e.g., chemical stability, ionic conductivity, ceramic integrity)
- Designing improvements to NaSICON through processing and composition to optimize performance for Na-based batteries

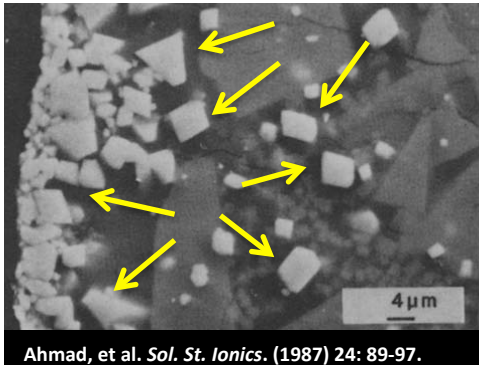
NaSICON Materials Chemistry

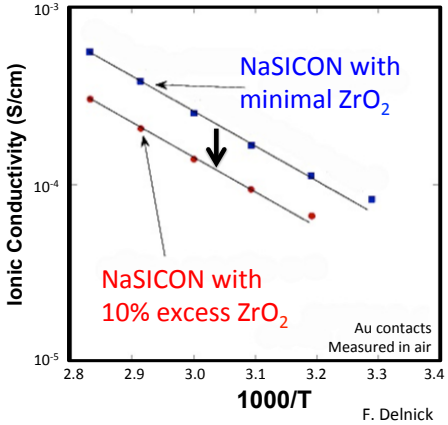
NaSICON performance depends on phase chemistry!

Secondary phase formation can have a significant impact on:

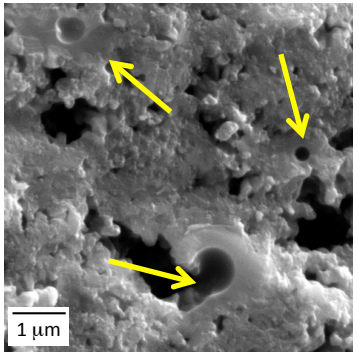
- *ionic conductivity*
- *structural integrity*
- *chemical stability*

ZrO_2 (monoclinic and tetragonal)

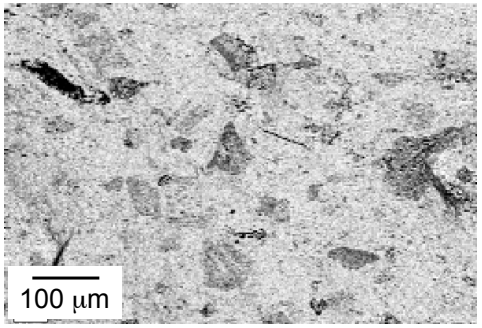




Glassy inclusions



Sodium silicates



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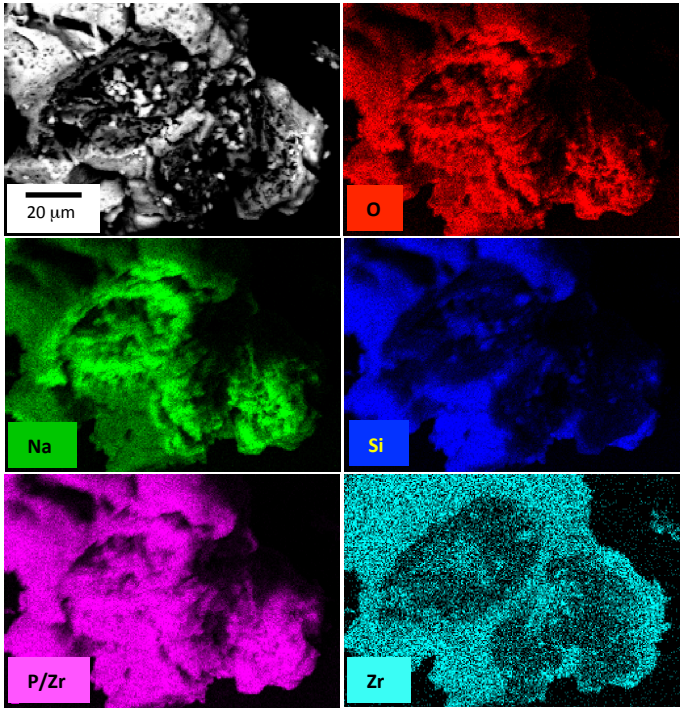
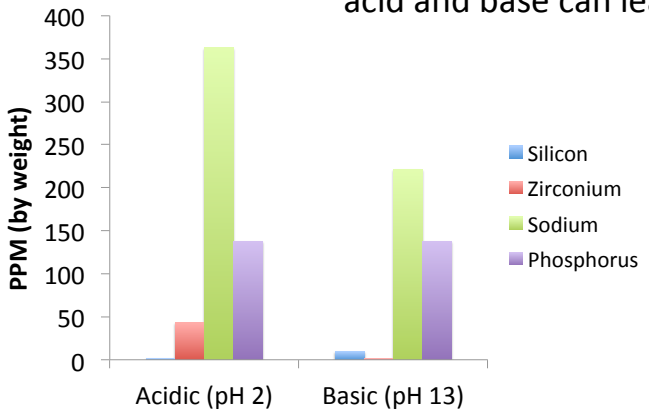
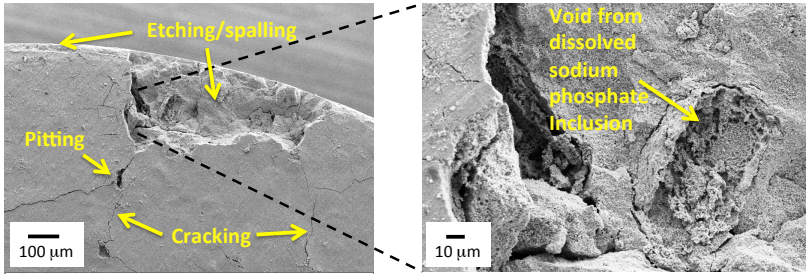
Sodium phosphates



High solubility of sodium phosphates in acid and base can lead to mechanical failure!



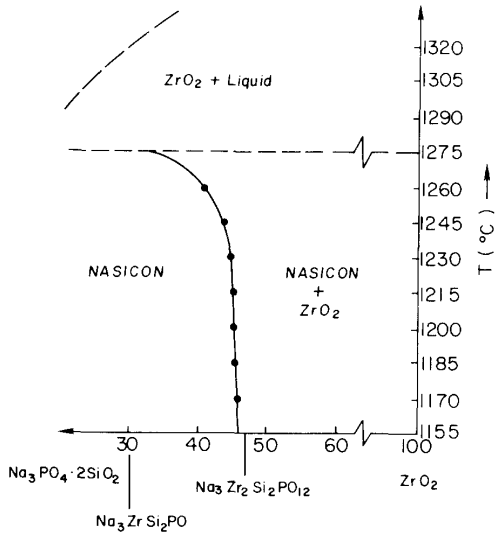


Phase Dependence on Processing

Phase composition of NaSICON depends on processing

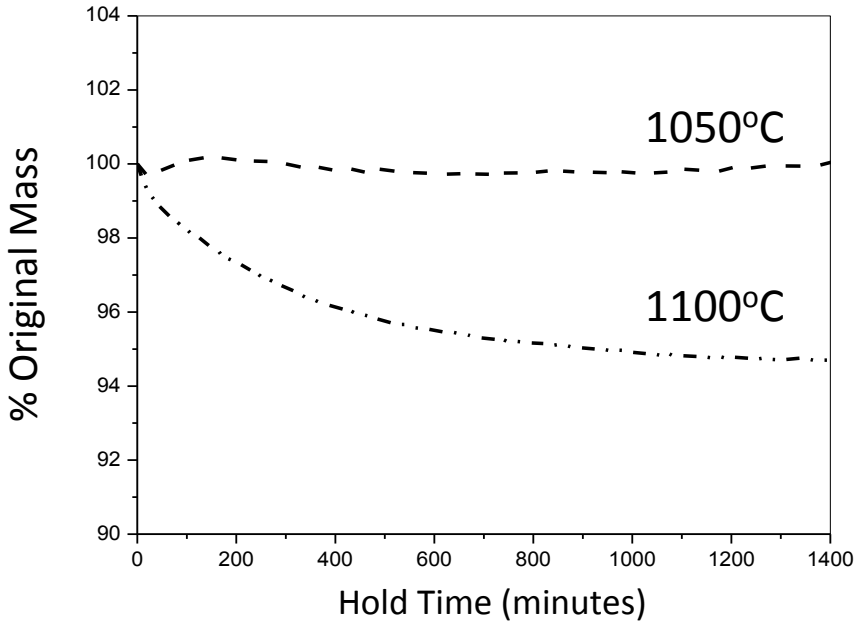
- Solid state processing of NaSICON ceramics typically involves an extended high temperature firing stage (>1200°C, >12 hours)

"Decomposition" of NaSICON



R.S. Gordon, *et al. Solid State Ionics.* ***3/4*** *(1981) 243-248.*

Loss of volatile species (e.g., Na and P)

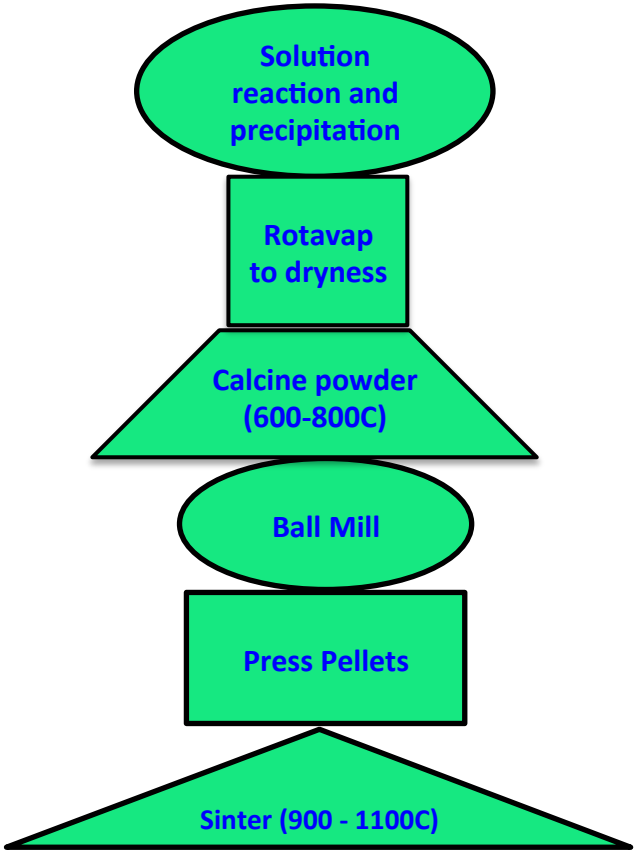


High temperature processing leads to deleterious secondary phases!

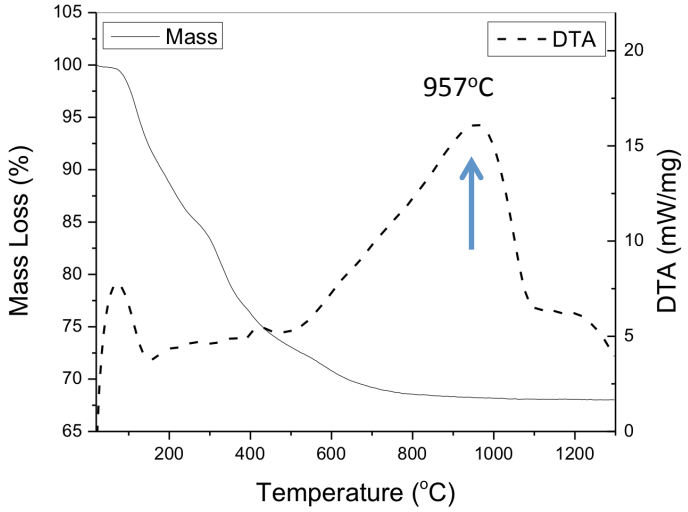
Will a lower temperature process resolve phase impurity?

“Low” Temperature Sol-Gel NaSICON

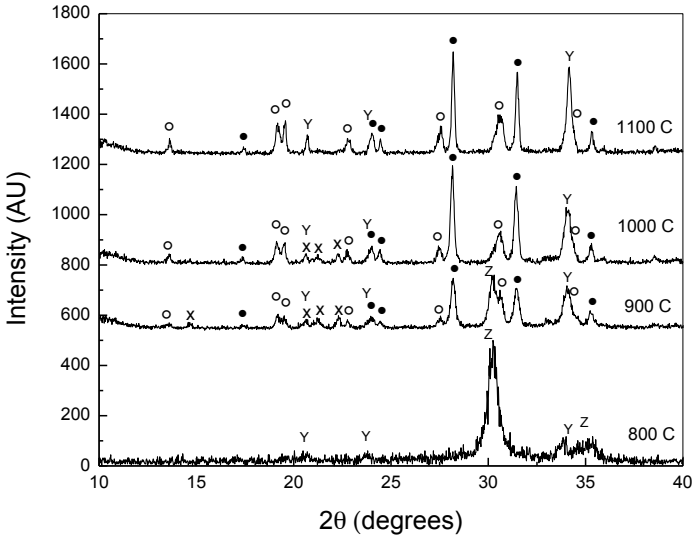
Sol-gel processing



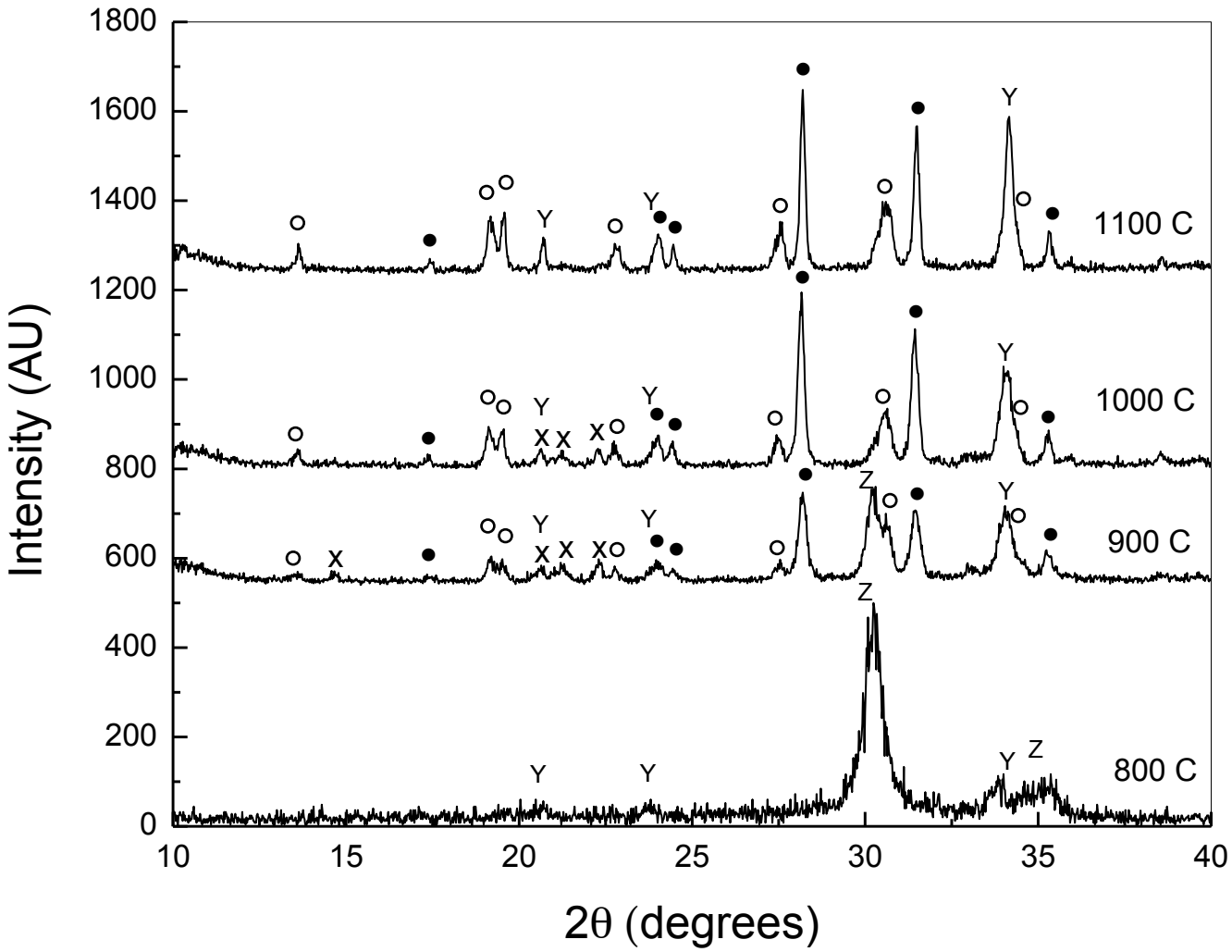
Thermal analysis identifies NaSICON formation temperature.



X-ray diffraction shows evolution of crystalline phases.



Sol-Gel NaSICON Phase Evolution



X-ray diffraction shows the presence of $Na_3Zr_2PSi_2O_{12}$ (o) *and*

- Tetragonal ZrO_2 (Z)
- Monoclinic ZrO_2 (•)
- Na_3PO_4 (Y)
- $Na_2Si_2O_5$ (X)

secondary phases.

Monoclinic ZrO_2 appears to form from conversion of metastable tetragonal ZrO_2.

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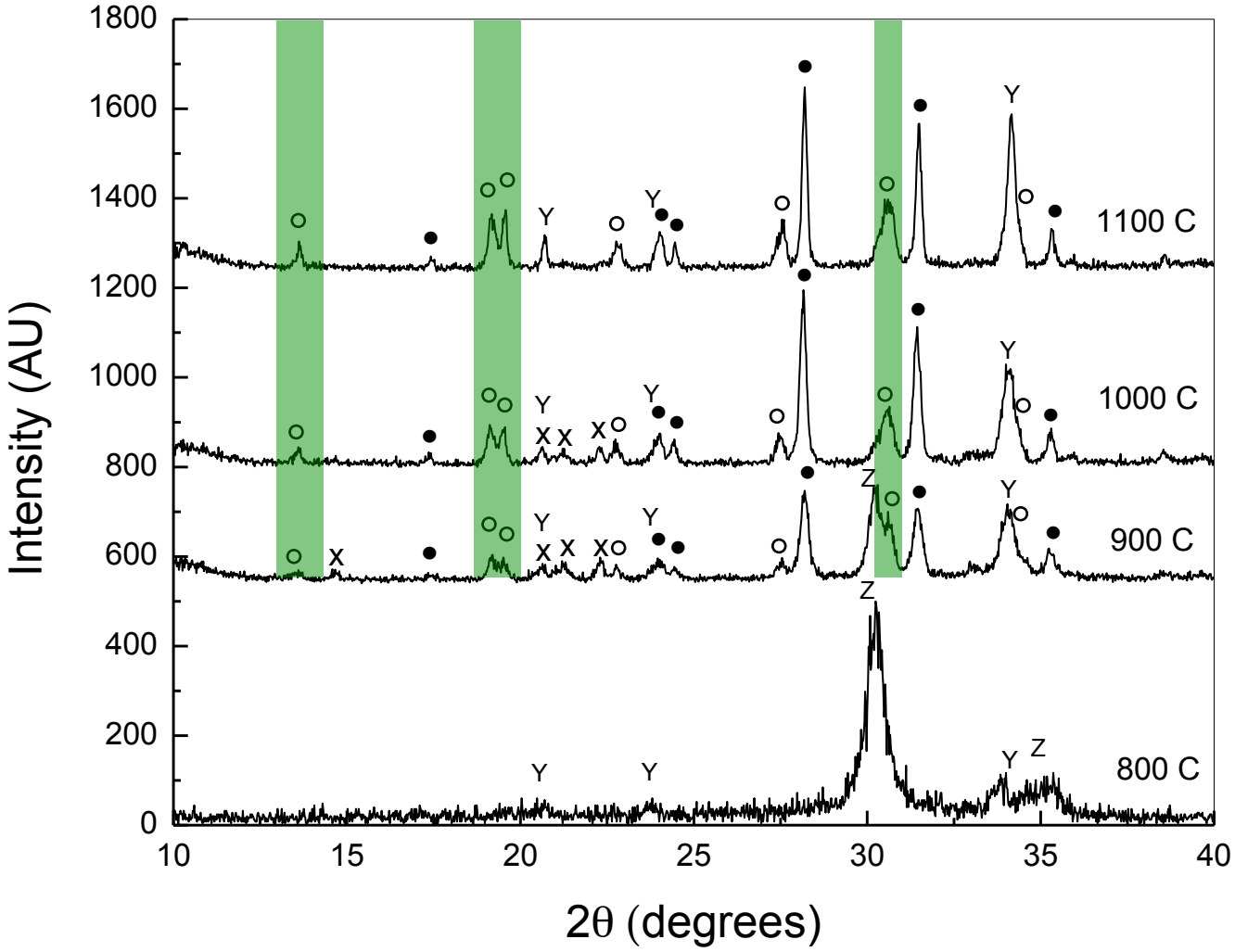

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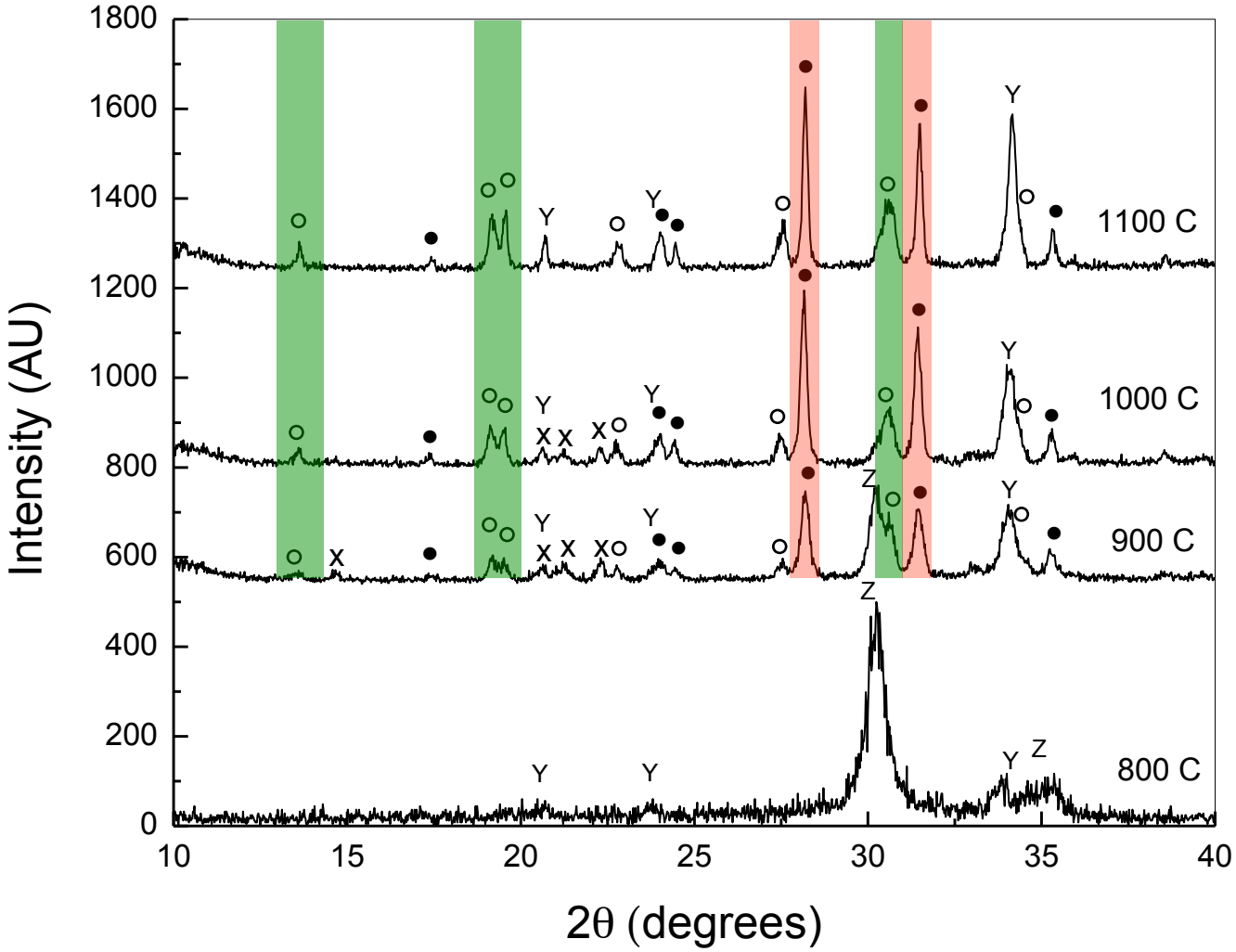

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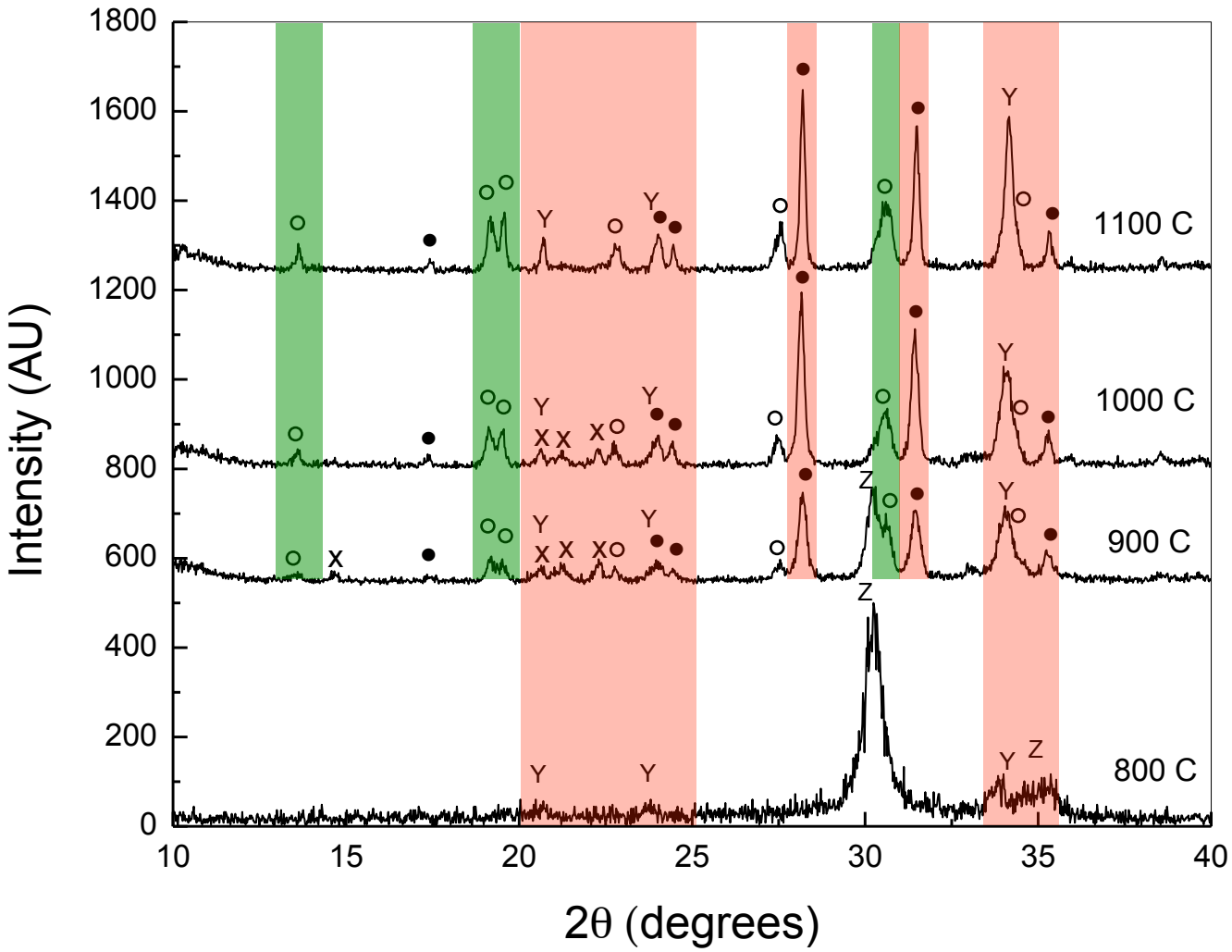

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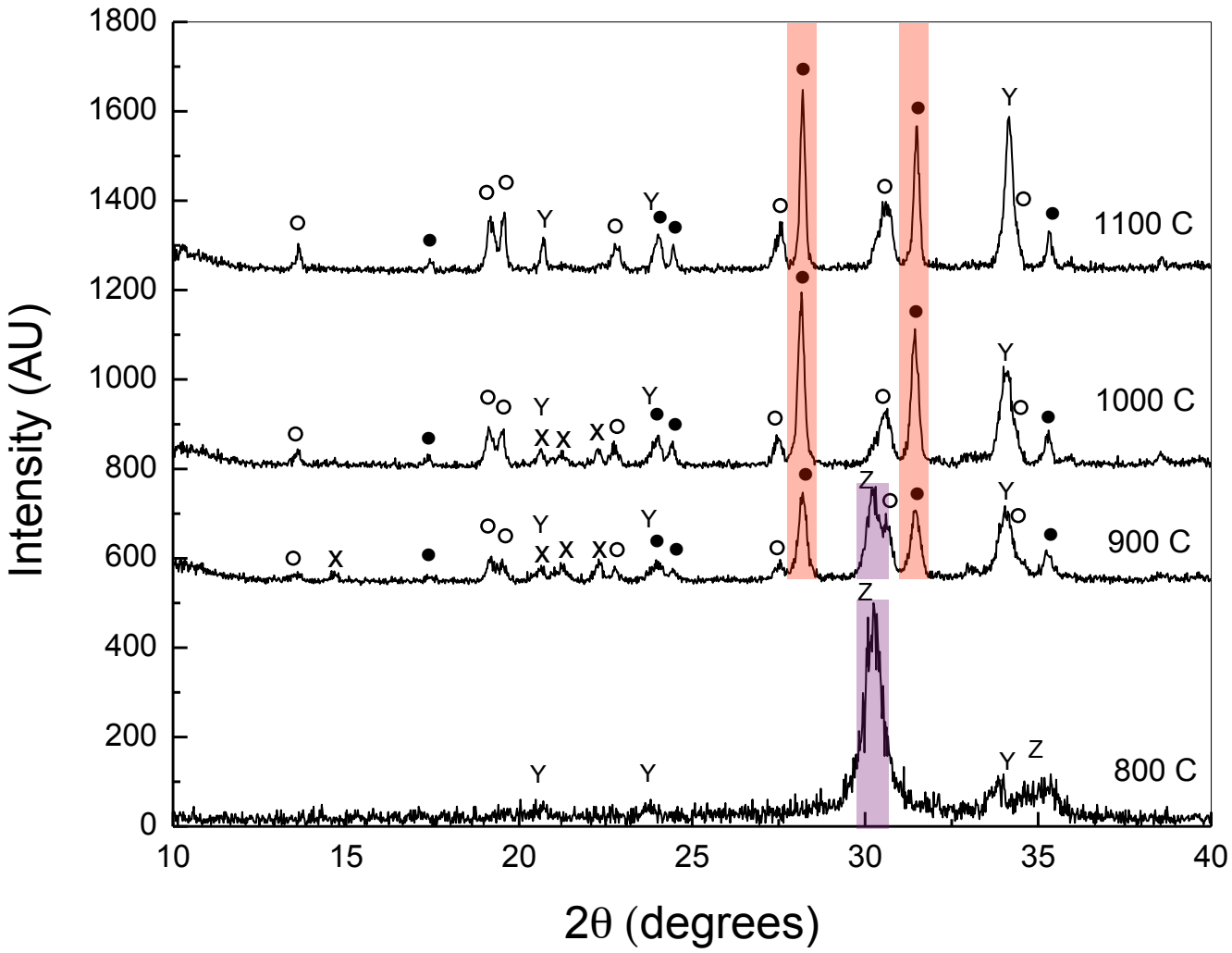

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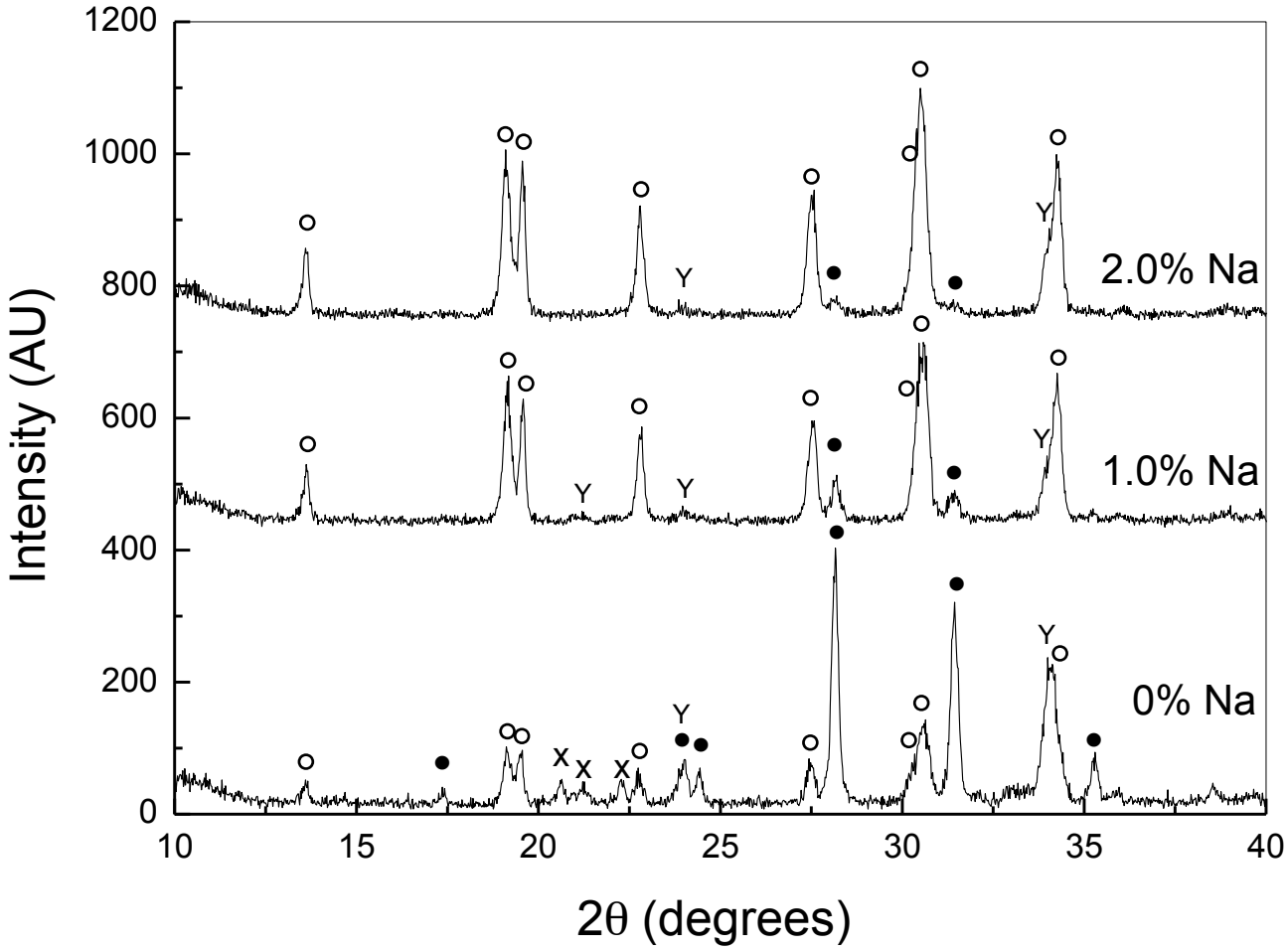
Lessons from Low Temperature Processing

- Phase evolution during heating is complex!
- Lower processing temperatures result in significant secondary phase formation.
- Secondary phase are not formed just from high temperature processes, but can be residual from incomplete low temperature conversions.
- Higher temperatures appear to be needed for complete phase conversion, but high T^{o}C is expected to lead to secondary phases.

What Next?

Excess Sodium Addition

NaSICON with excess sodium fired at 1000°C shows dramatically cleaner phase chemistry!



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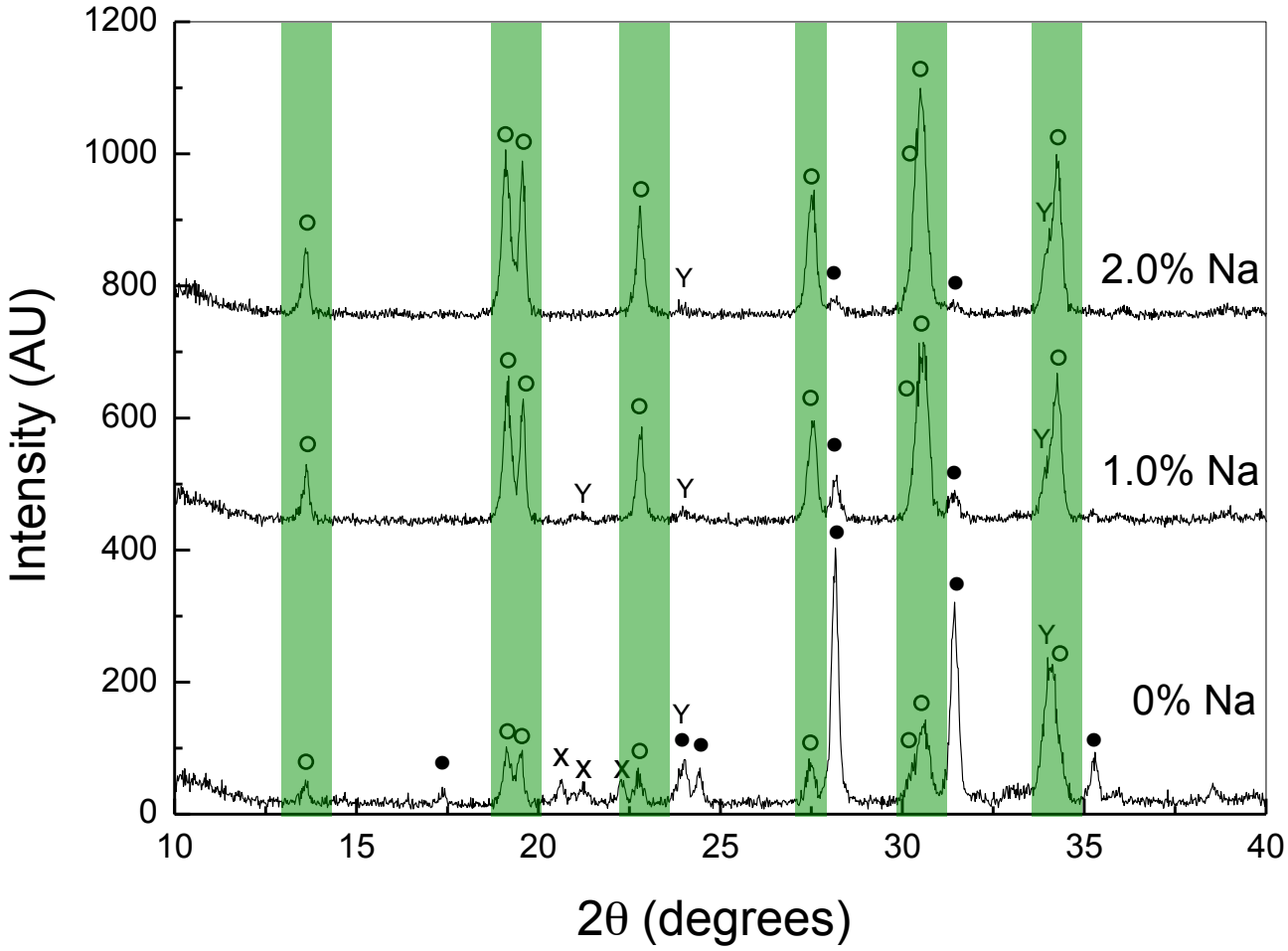

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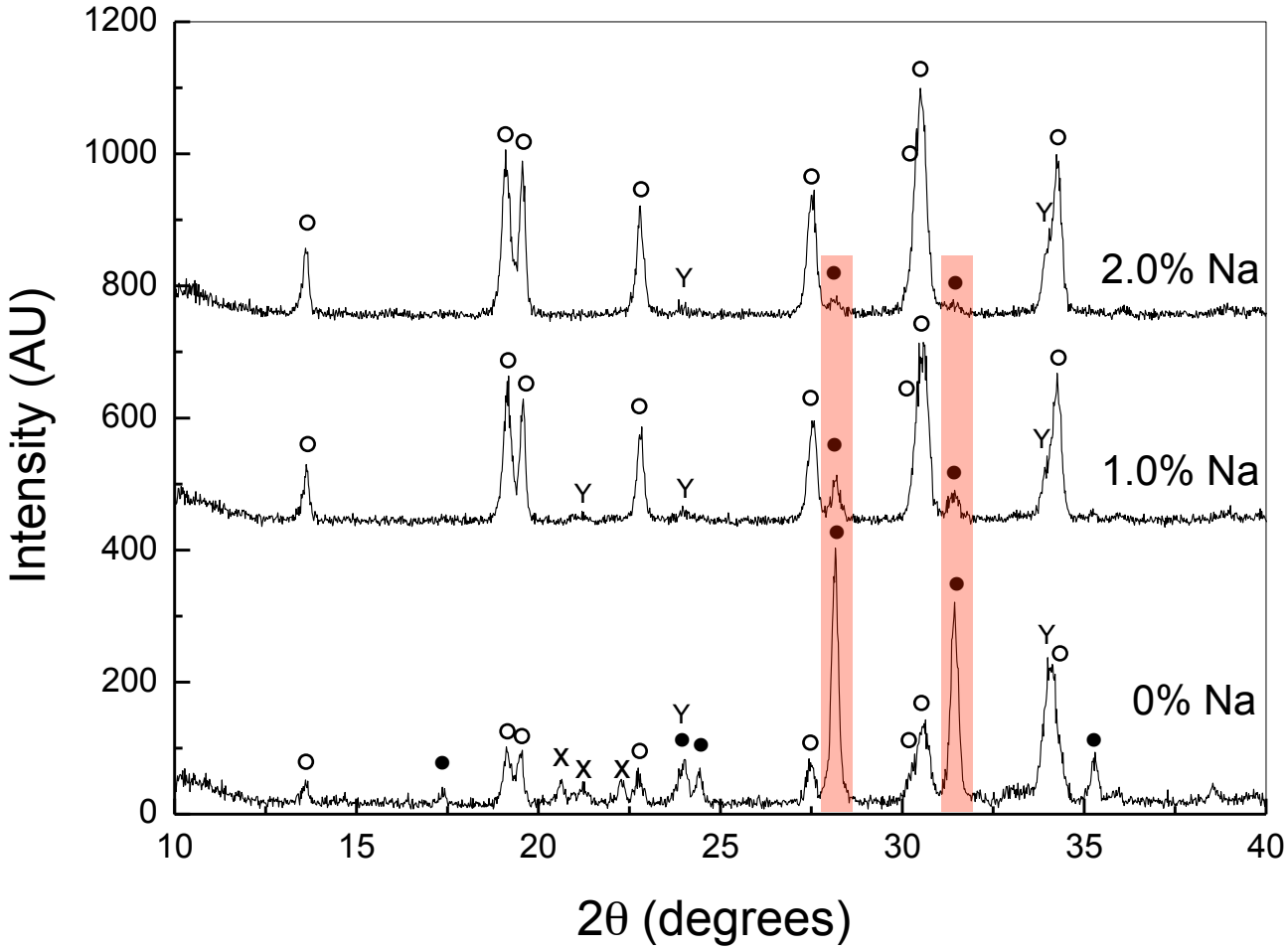
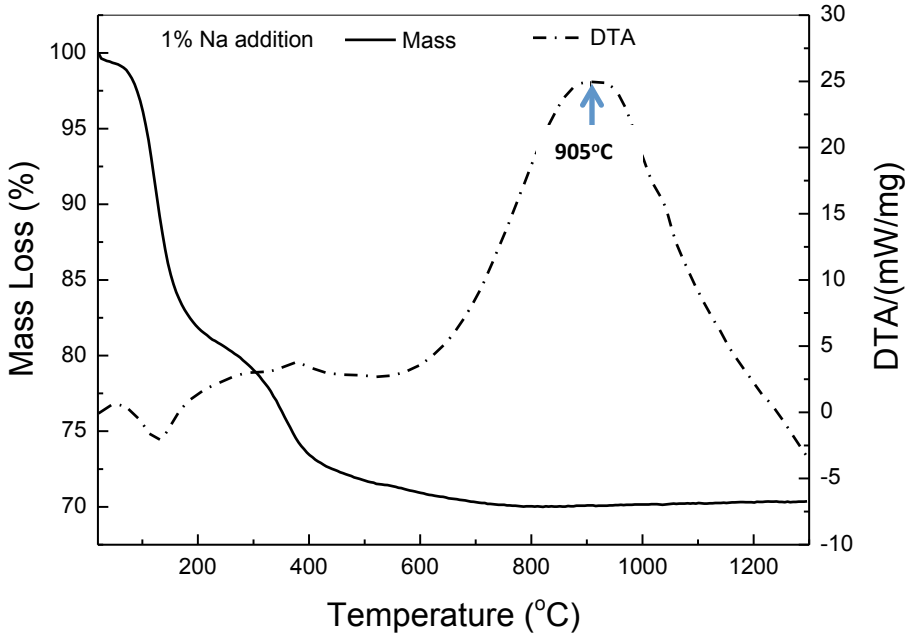
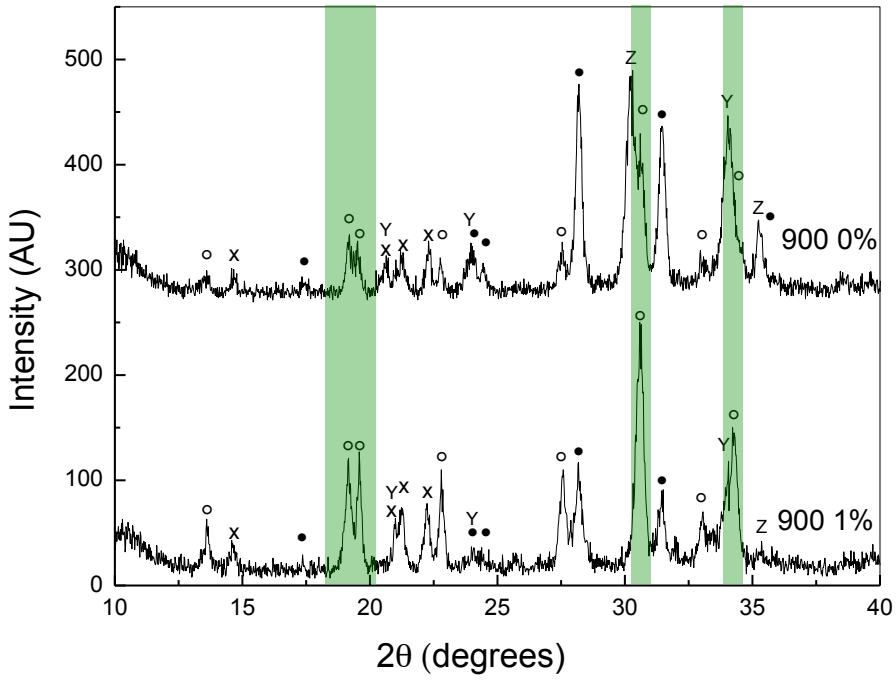


Excess Sodium Reduces Effective Processing Temperature

Thermal Analysis and XRD show NaSICON formation at lower temperatures with excess Na!





Excess sodium addition appears to change the energetics of NaSICON conversion, likely by affecting mass transport in liquid phase elements of sintering.

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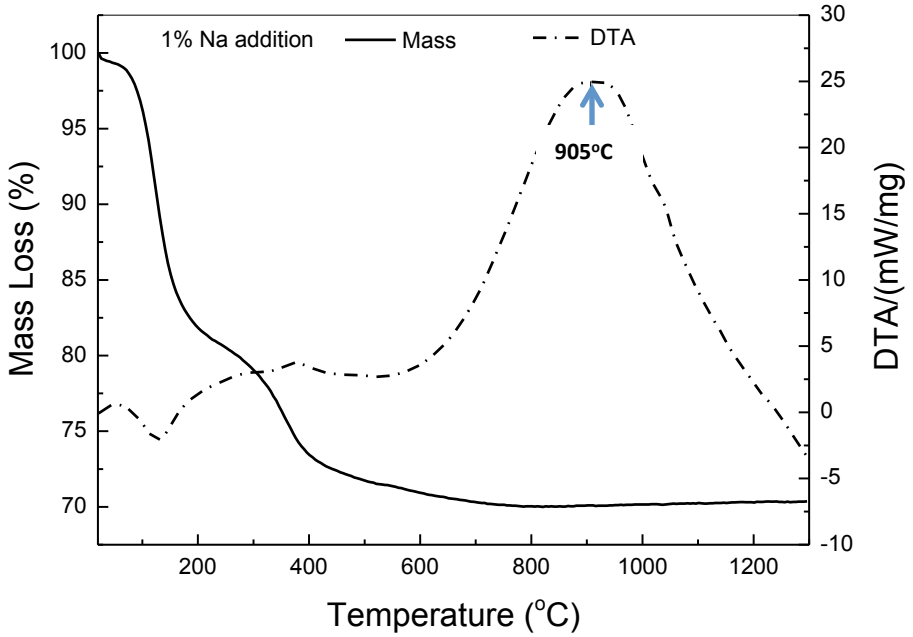

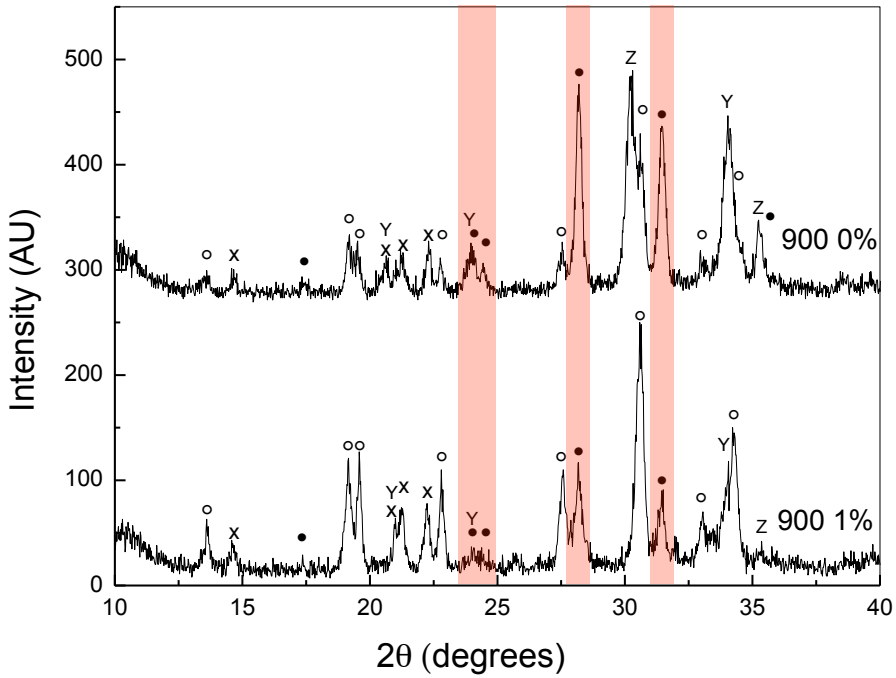

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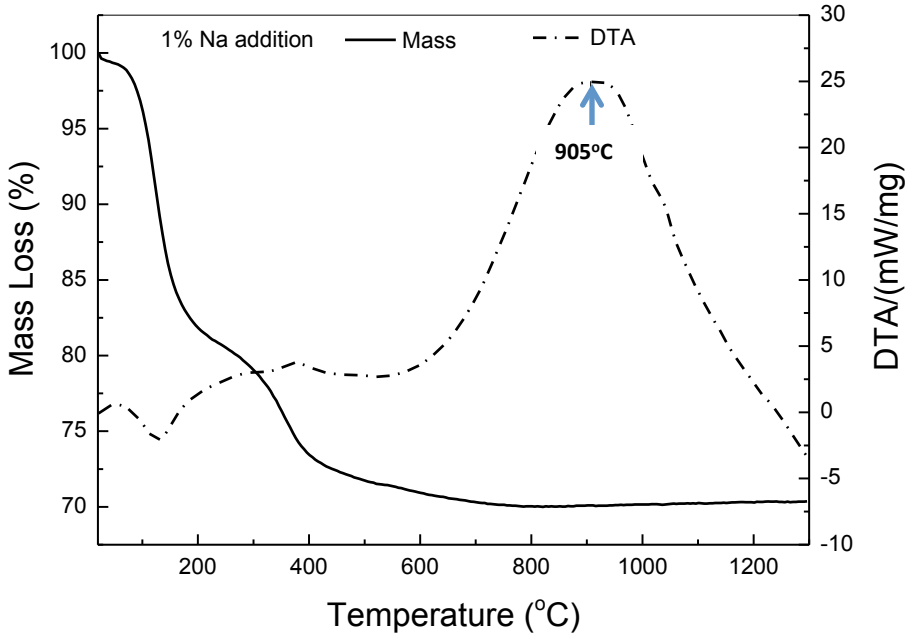

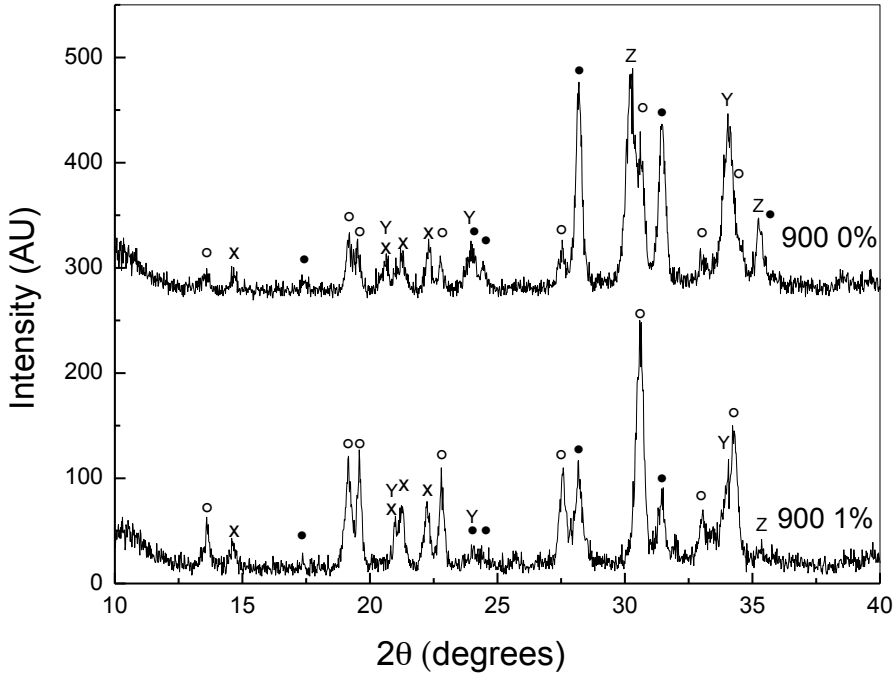

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Wrapping Up…

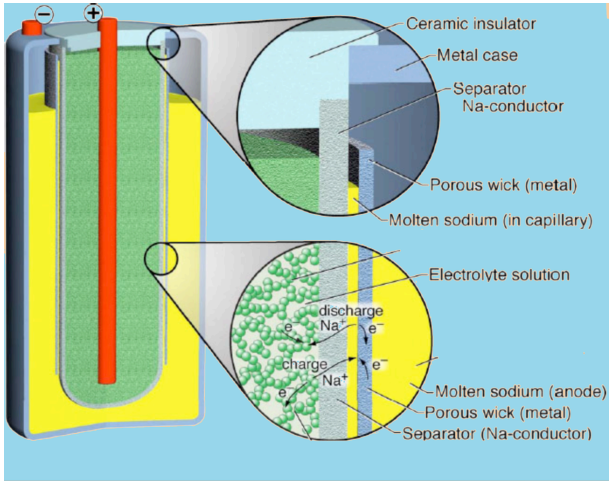
What have we learned?

- NaSICON ceramics are promising solid state electrolytes for Na-based batteries.
- Controlling secondary phase chemistry is critical to optimizing NaSICON performance.
- Reducing processing temperatures does not improve NaSICON phase purity.
- **Addition of small amounts of excess sodium dramatically reduces secondary phase formation at lower temperatures!**

Looking Forward

Targeting synthesis of improved NaSICON stability to enable integration into next generation Na-based batteries:

- Explore alternative mechanisms to reduce processing temperatures with high phase purity.
- Investigate alternative precursor pathways to control phase chemistry.
- Evaluate effects of phase chemistry on sodium ion transport/conductivity.
- Examine chemical stability of NaSICON as affected by additives (such as sodium).
- Study the relationships between phase chemistry and microstructure (e.g., grain structure) with respect to NaSICON performance.



Acknowledgements

Thank you!

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