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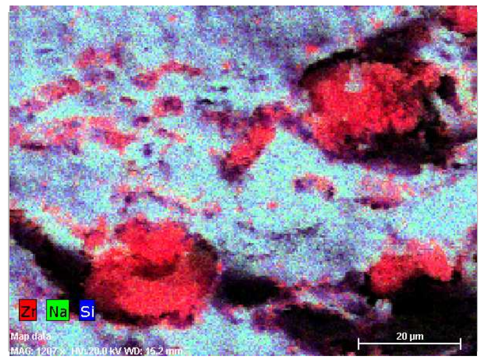

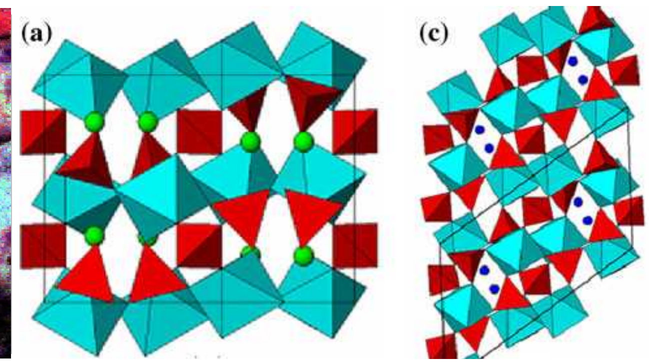

Phase Development and Densifi
NaSICON Ceramics

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Motivation and Overview

- Nasicon ceramics are leading compositions in sodium ion conduction, yet suffer from several processing difficulties in manufacturing dense membranes.

- This work examined Nasicon ceramics formed using a molecular precursor approach, and examined densification of materials ranging from the pure phosphorous composition to the pure silica composition.

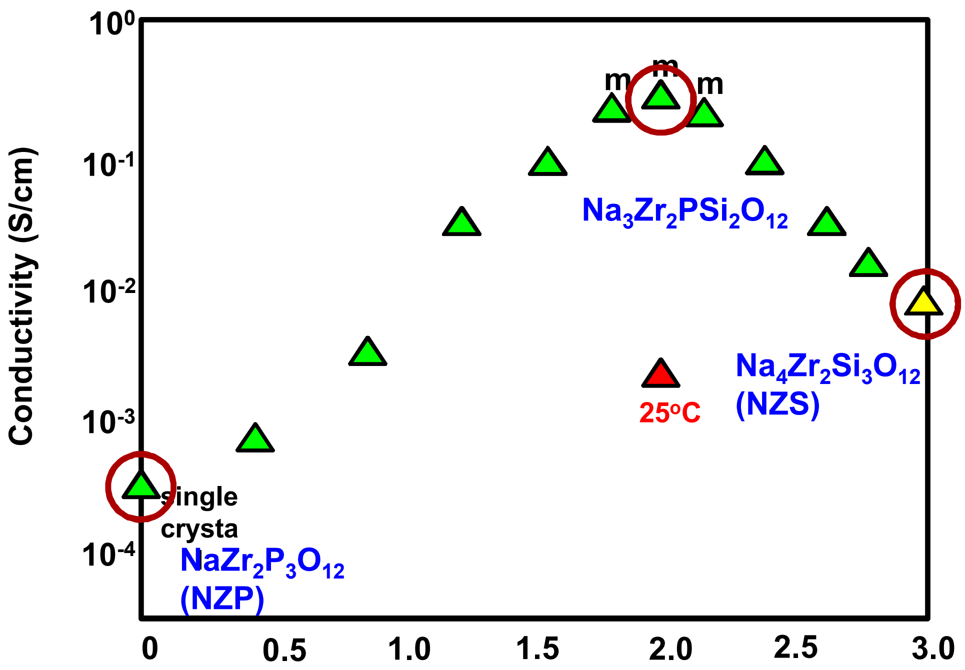
- Variation in sintering densification, grain growth, and phase stability were characterized by SEM, XRD, and compositional mapping with EDS.

A NaSICON Primer…

Baseline Compositions: $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (NZP = $NaZr_2P_3O_{12}$, NZS = $Na_4Zr_2Si_3O_{12}$)

Ionic Conductivity of NASICON

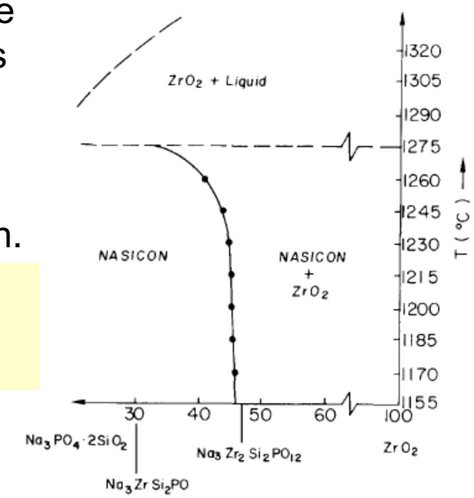
$Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, 300°C
(rhombohedral, except m = monoclinic)



Zr sites: all octahedral
P, Si sites: all tetrahedral
O sites: all bridging (octahedra to tetrahedra)

- High temperature processing leads to non-stoichiometric liquid phase and phase separation.

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



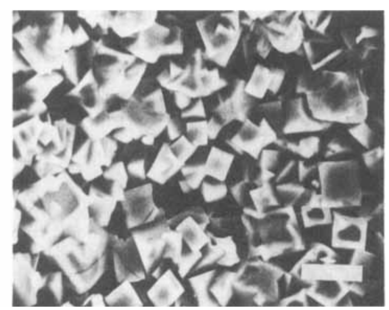


Fig. 2. Nasicon grain structure, showing intragranular microcracks (bar=10 μm).

B.J. McEntire, et al. *J. Am. Ceram. Soc.* **66** (1983) 738.

- ZrO_2 segregation is common to high temperature processed NaSICON, due to Na + P volatility and glass phase formation.

Synthetic Strategy: A Molecular Precursor Approach

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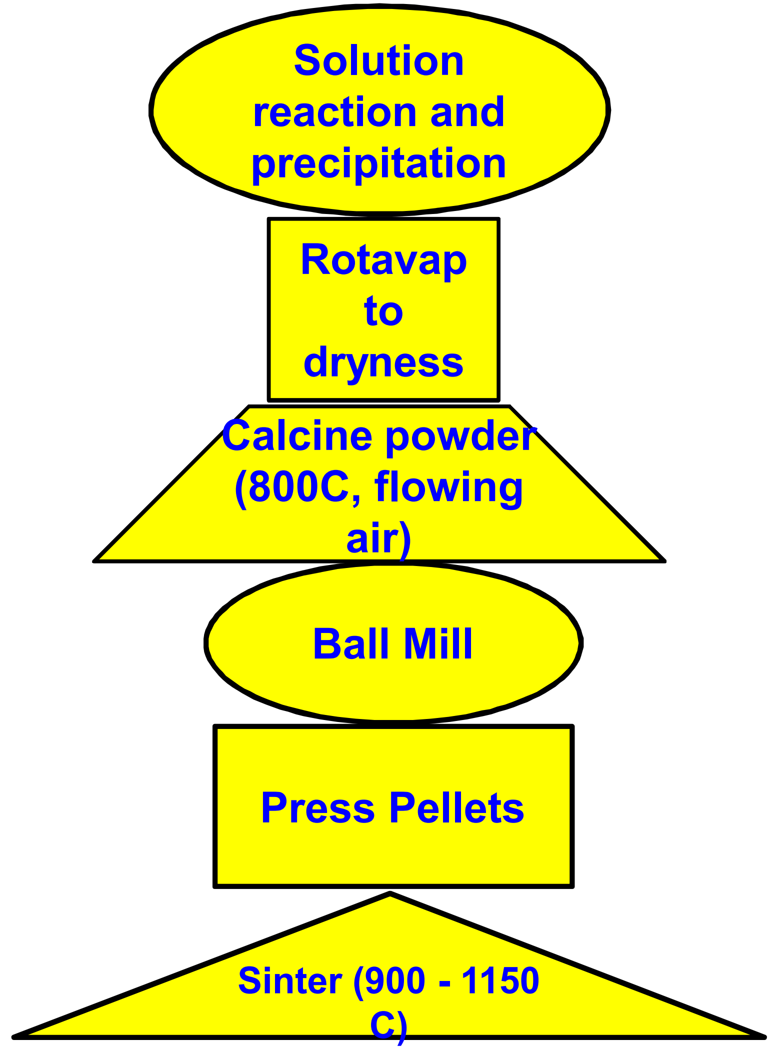
Most published syntheses use multistage "sol-gel"chemistry – can be tricky because not all of NASICON's components react simultaneously!

We have adopted a process that combines all the reagents as an intimately mixed multicomponent "gel" that we can calcine and fire.

- **$NaZr_2P_3O_{12}$:** NaOH (excess Na-Acetate); pyrophosphoric acid, chelated zirconium alkoxide complex; rotavap to powder; calcine; ball mill; press pellets; sinter (900-1150C)

- **$Na_4Zr_2Si_3O_{12}$:** NaOH (excess Na Acetate); TEOS, chelated zirconium alkoxide complex; rotavap to powder; calcine; ball mill; press pellets; sinter (900-1150C)

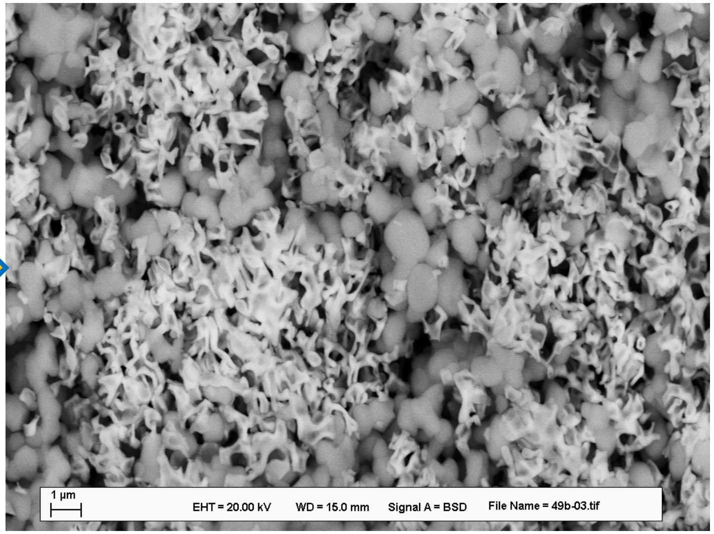
- **$Na_3Zr_2PSi_2O_{12}$:** Trisodium phosphate (excess Na Acetate), TEOS; rotavap; add Zirconia acetylacetonate complex; rotavap to powder; calcine; ball mill; press pellets; sinter (900-1150C)



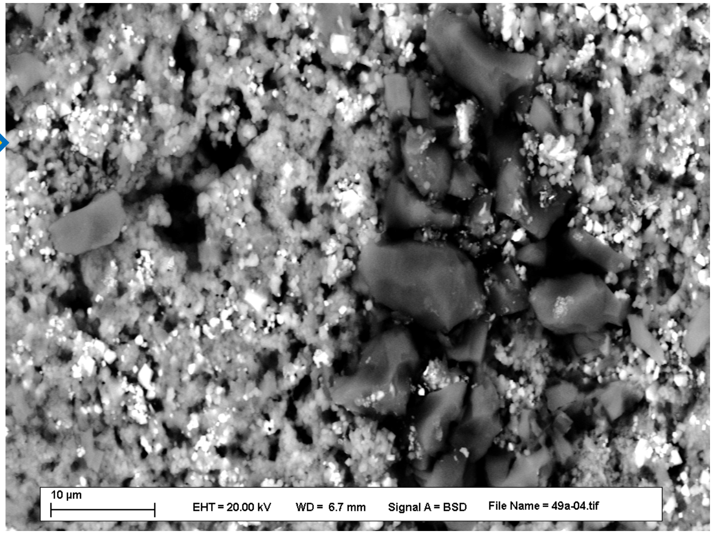
Porkodi et al., *Chem. Mater,* **20** (2008) 6410.

Why can't you Sinter at higher temperatures?

- Sintered at 1150 °C, 12 hr
- $NaZr_2P_3O_{12}$
- Samples were ball milled, and pressed at 40 ksi

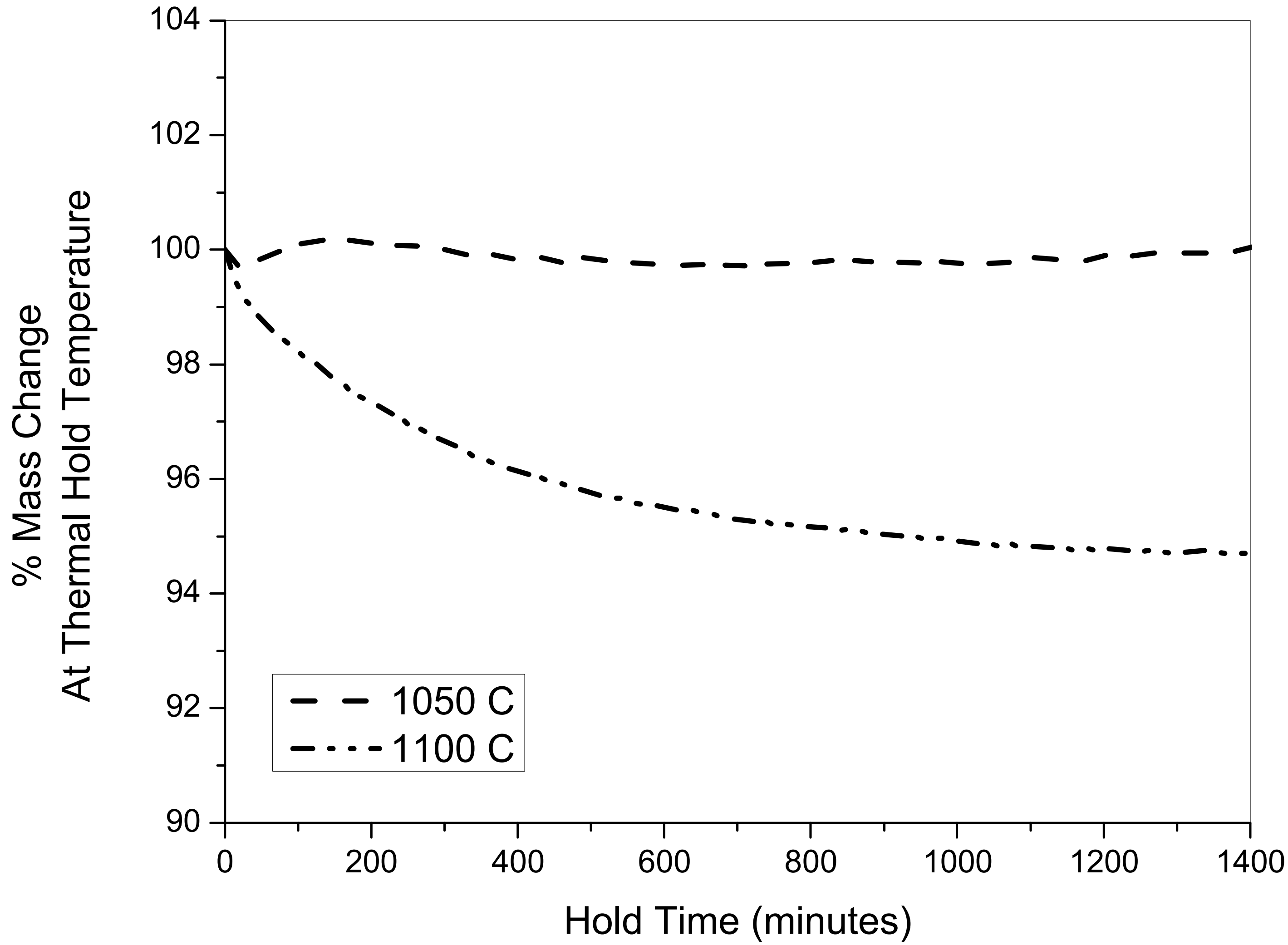


- $Na_3Zr_2PSi_2O_{12}$



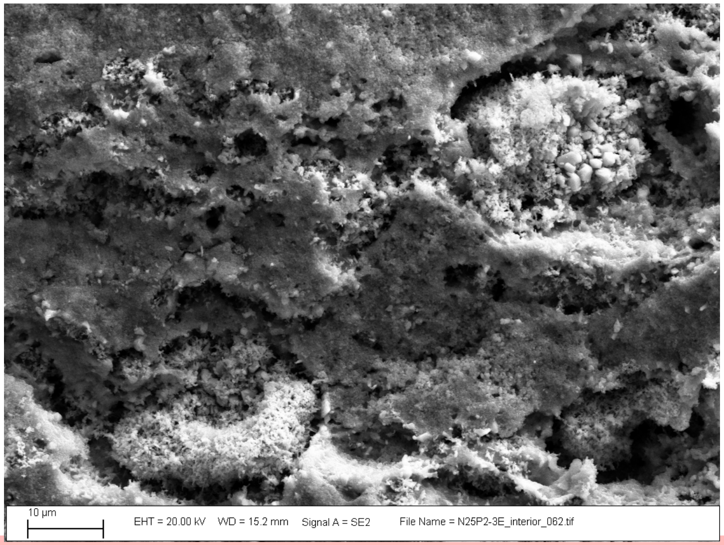
- Sodium volatility is significant at high temperatures.

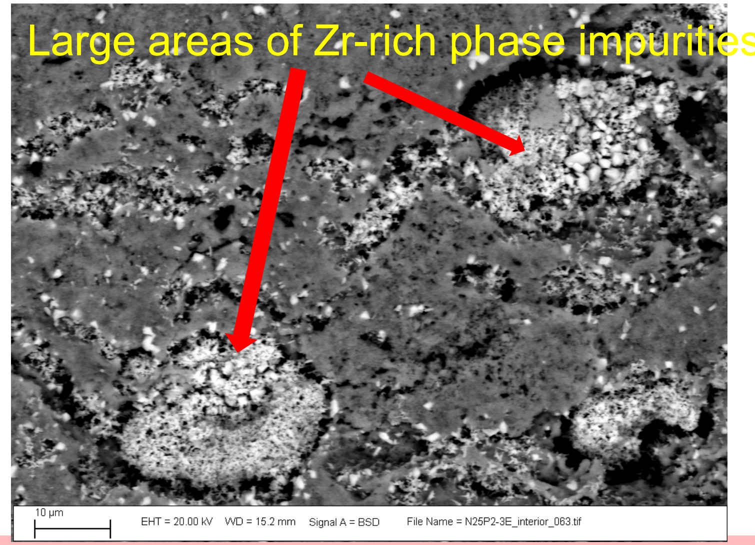
Na & P Volatility sets an upper thermal boundary below 1100 °C.



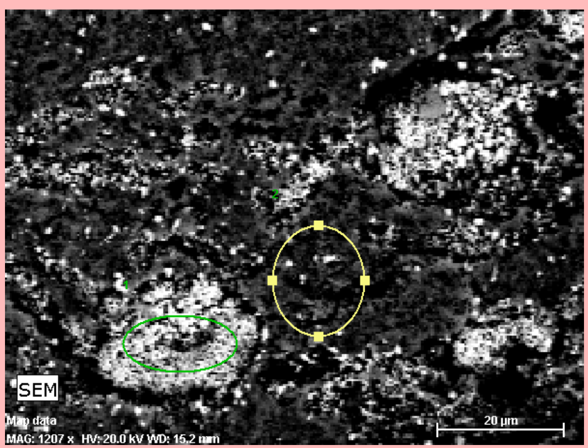
Inhomogeneities in Pellets

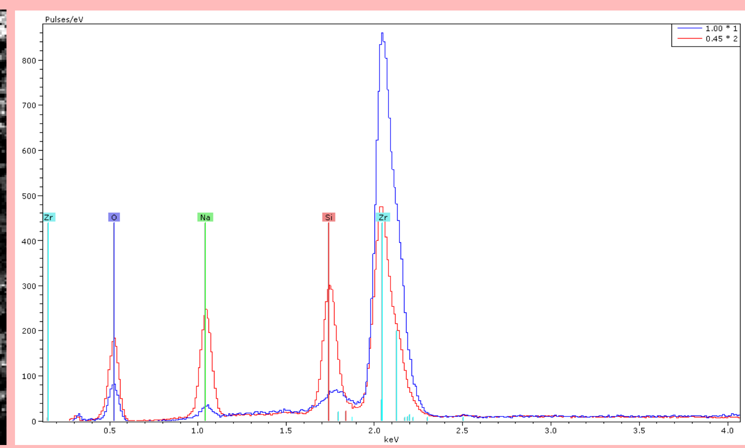
$Na_3Zr_2PSi_2O_{12}$, Fired at 1100 °C



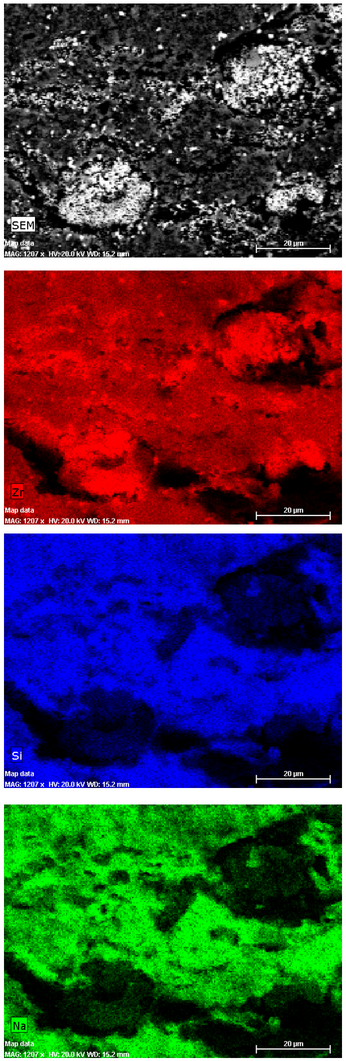


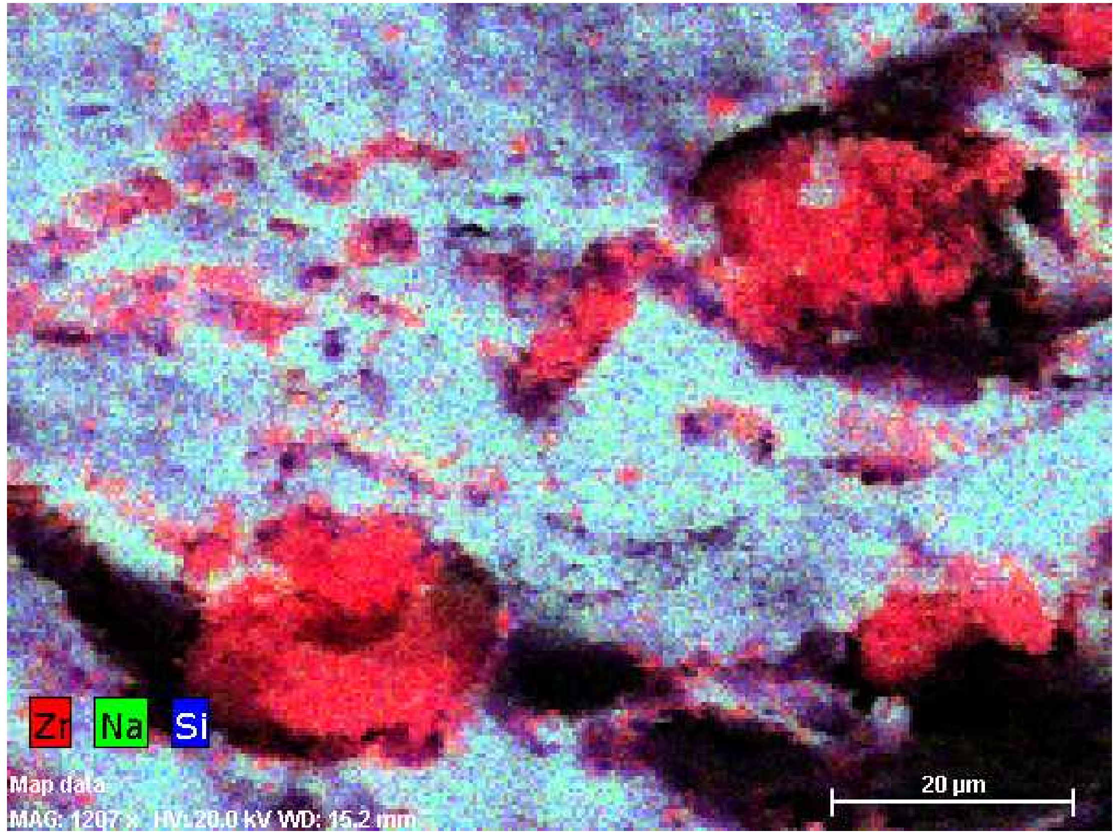
EDS Mapping was used to identify phase non-uniformities in the fracture surfaces. Signals normalized to background.





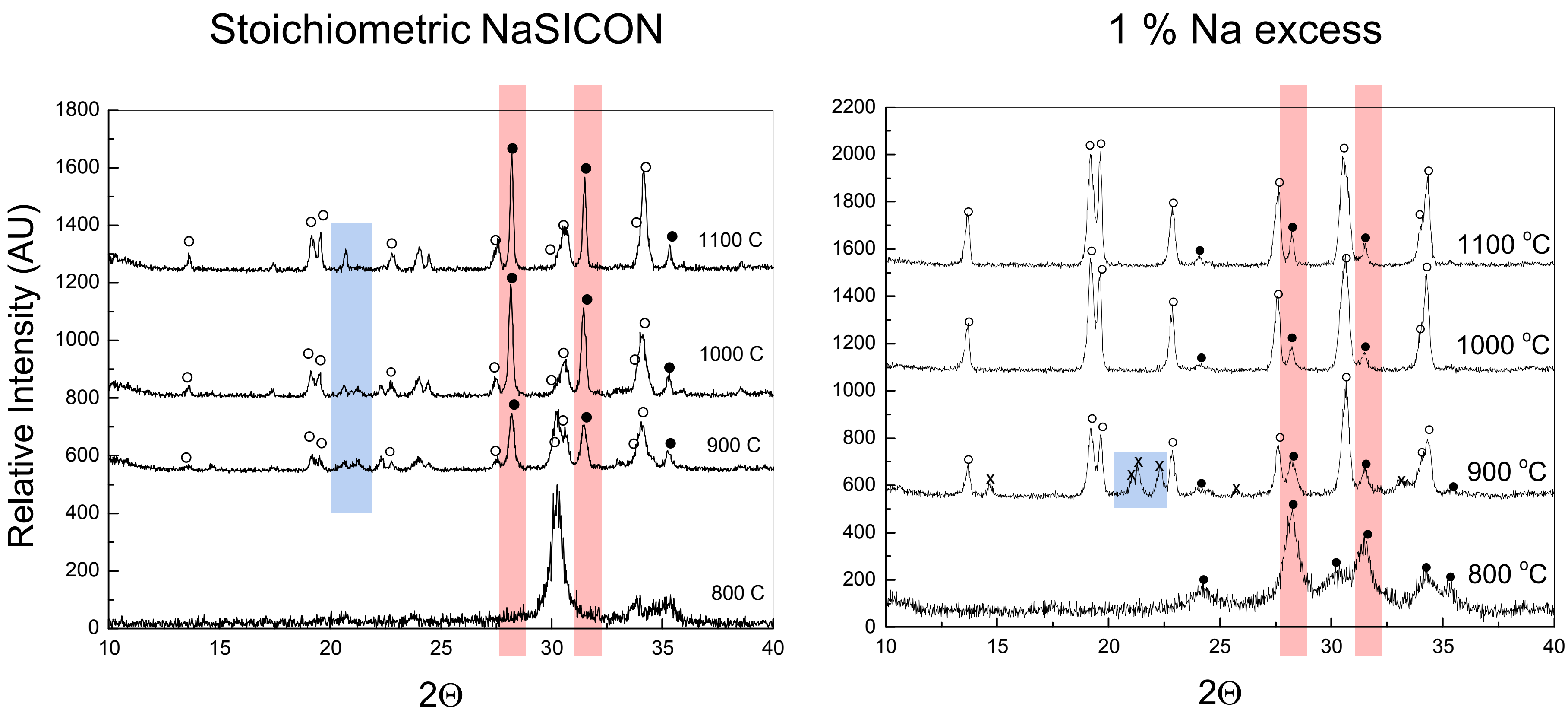
$Na_3Zr_2PSi_2O_{12}$, 1100 °C, EDS Map





EDS overlay shows phase impurity regions are Zr rich, and deficient in Na and Si, and are likely a doped ZrO_2 material.

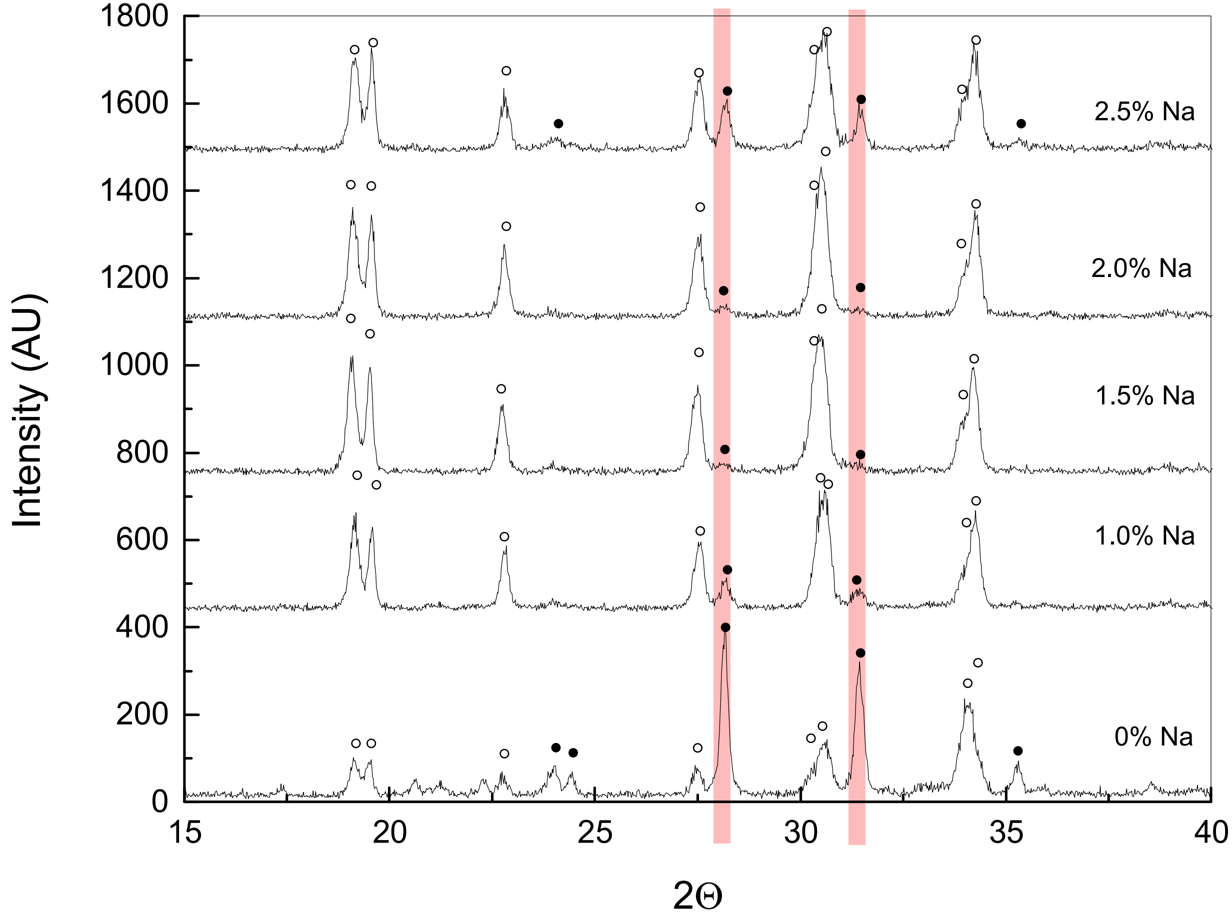
Excess Na has a dramatic effect on phase uniformity



Monoclinic ZrO_2 peaks (•), Nasicon Peaks (∘), and $Na_2Si_2O_3$ (x).

Phase pure NaSICON requires firing above 900 °C to eliminate the $Na_2Si_2O_3$ phase, as well as excess Na to minimize the Zirconia phase.

Na Content is most effective in a small range at 1000 °C.



Optimal phase purity found for Na excess between 1 and 2 mole%.

Monoclinic ZrO_2 peaks (•), Nasicon Peaks (∘), and $Na_2Si_2O_3$ (x).

1 % Excess Na lowers the Crystallization Temperature of NaSICON

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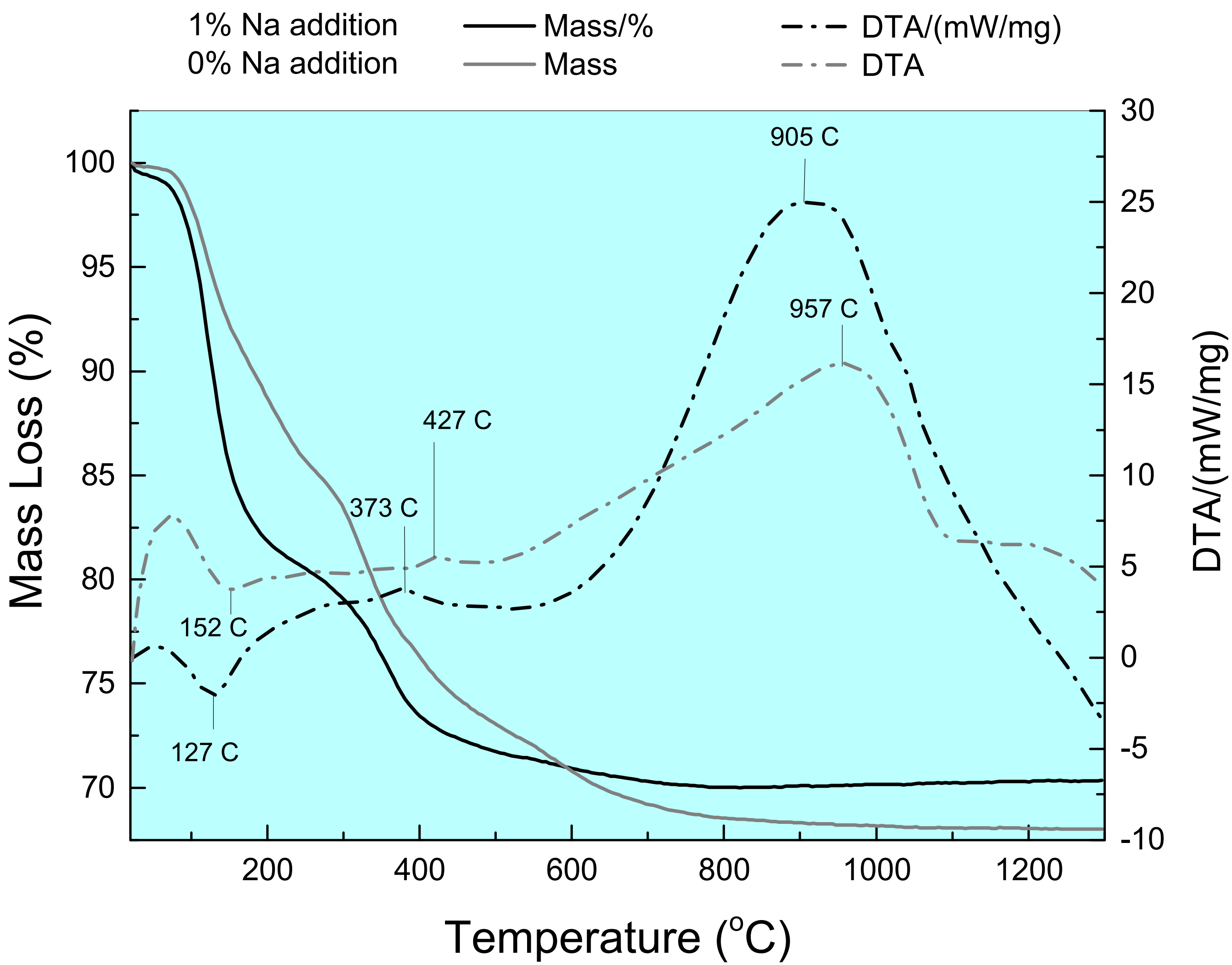

- Tetragonal ZrO_2 formed during calcination.
- NaSICON crystallizes above 900 °C.
- Excess Na:
  - Promotes growth of NaSICON phase.
  - inhibits growth from initial ZrO_2.
  - Increases dissolution of ZrO_2.

NaSICON Densification

- Reactive powders (sol-gel) require temperatures of 1125 – 1325 °C for densification [A.K. Kuriakose et al. *J. Am. Ceram. Soc.* **67** (1984) 179.]
- Density for 1 Mol% Excess Na compositions vs. Temperature (12 hr hold time)

Composition	900 °C	1000 °C	1100 °C
$Na_{1.01}Zr_2P_3O_{12}$	1.89 g/cc (59% TD)	3.21 g/cc (100%TD)	3.21 g/cc (100%TD)
$Na_{3.03}Zr_2PSi_2O_{12}$	2.54 g/cc (77.9% TD)	2.70 g/cc (82.8% TD)	2.87 g/cc (88.1% TD)
$Na_{4.04}Zr_2Si_3O_{12}$	2.15 g/cc (63.9% TD)	2.92 g/cc (86.8% TD)	3.04 g/cc (90.4% TD)

The NZP composition shows the best densification, whereas the optimal Na conductivity composition (PSi_2) shows the poorest sintering properties at low temperatures.

Densification at 1100 °C Gives ZrO_2 Inhomogeneity

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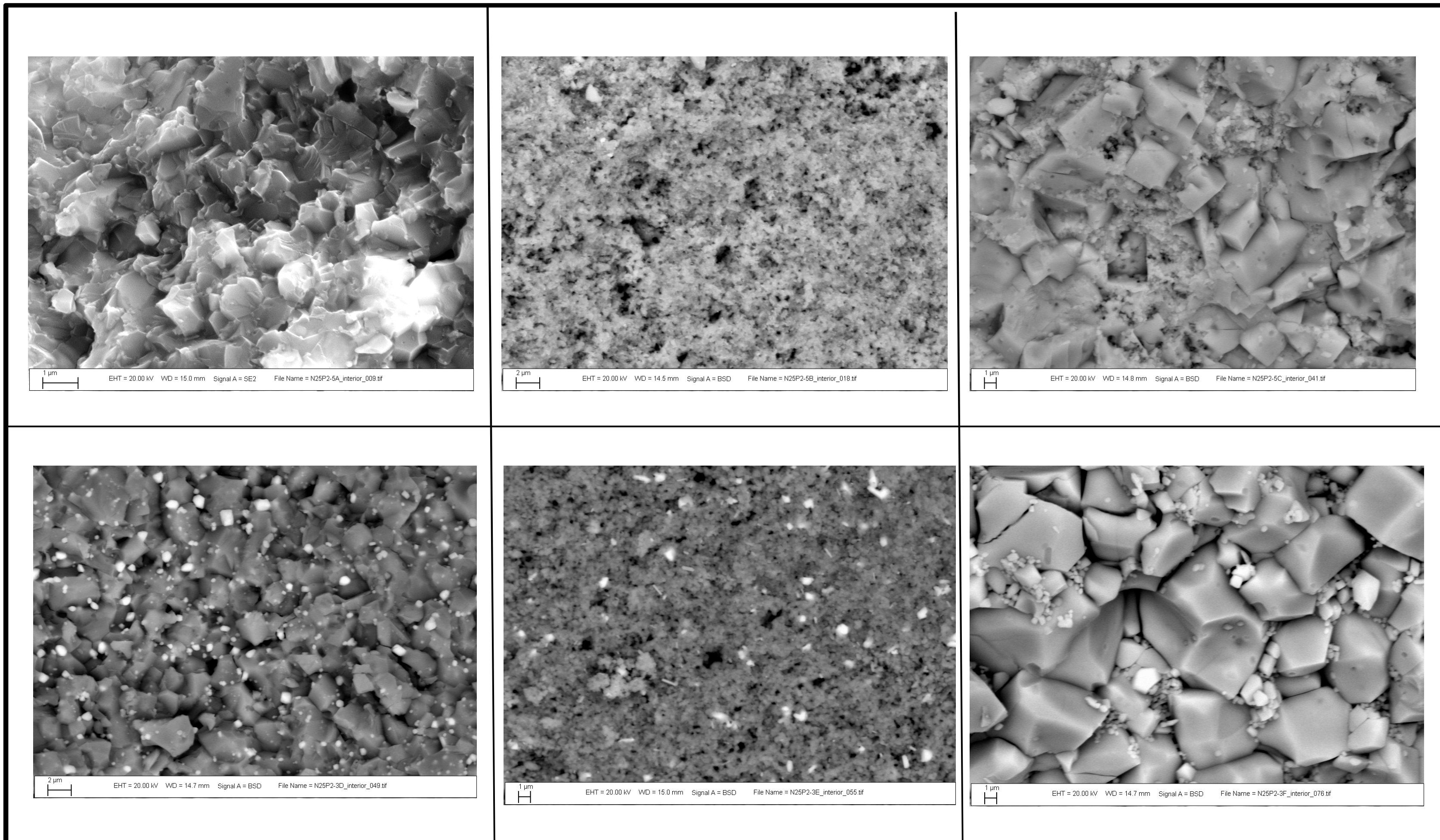
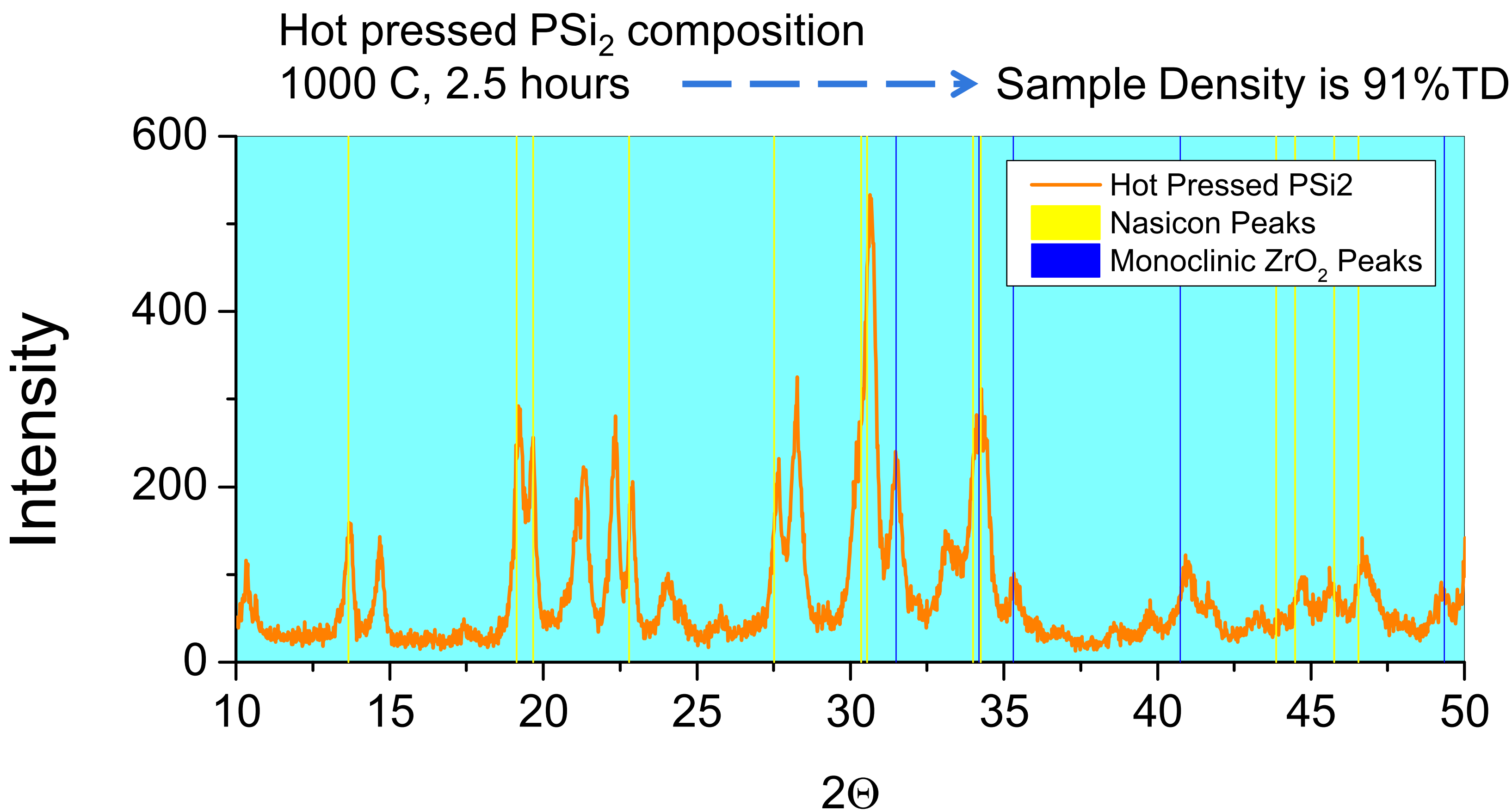
	$NaZr_2P_3O_{12}$	$Na_3Zr_2PSi_2O_{12}$	$Na_4Zr_2Si_3O_{12}$
1000 °C			
1100 °C			



Hot Pressing PSi_2 Composition at 1000 °C Densifies, but Phase Purity Suffers



- *The shorter duration may lead to the segregation of ZrO_2 as indicated by the XRD spectra.*
- *The anaerobic atmosphere may play a role as well.*

Summary

- There is a narrow thermal window for synthesis of dense NaSICON Ceramics.
  - Phase pure, crystalline NaSICON ceramics requires reaction at 1000 °C or above.
  - High temperature processing of Nasicon ceramics have a boundary of less than 1100 °C for phase pure, stoichiometrically controlled components.
- Sol-gel Produced powders can achieve near phase pure compositions using only 1-2 Mole % Na excess compositions.
- Densities are greatly affected by annealing temperature.
  - $NaZr_2P_3O_{12}$ at 1000 °C we have density >95% and phase purity
  - $Na_4Zr_2Si_3O_{12}$ at 1100 °C have ~ 90% density.
  - $Na_3Zr_2PSi_2O_{12}$ at 1100 °C has < 90% density, with minor ZrO_2 phase.
- *Each phase requires specific tailoring of chemistry to define phase space.*