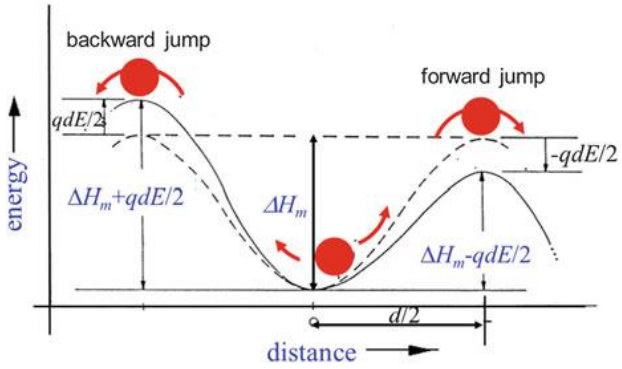
Karlsruher Institut für Technologie

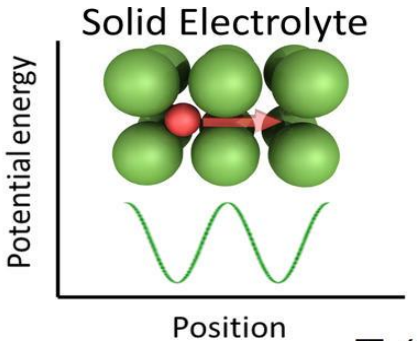
POLiS Post Lithium Storage Cluster of Excellence

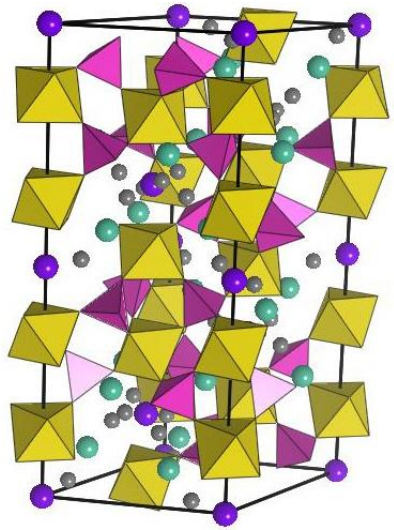
Thermophysikalische Eigenschaften von keramischen Feststoffelektrolyten

M. Rohde

INSTITUT FÜR ANGEWANDTE MATERIALIEN– ANGEWANDTE WERKSTOFFPHYSIK (IAM-AWP)

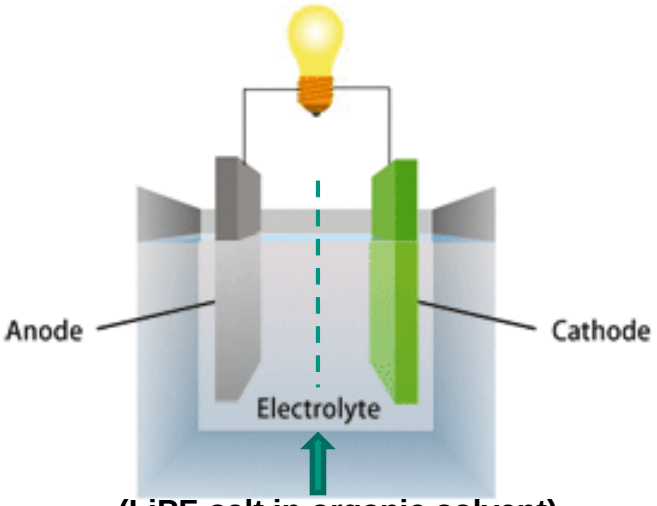






Solid electrolyte for Li-ion cells

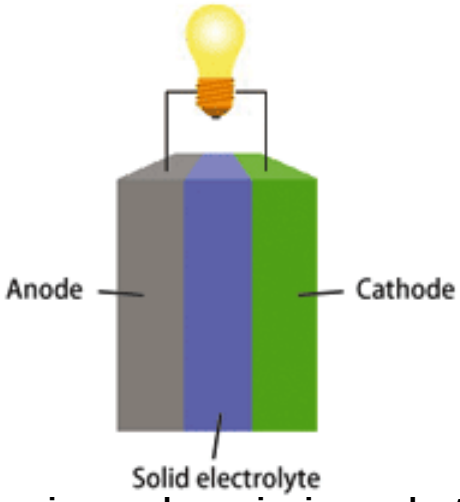
conventional cell



(LiPF-salt in organic solvent)

- security issues
- very reactive components
- restricted temperature range
- thermal runwaway
- exothermal degradation

all solid state cell



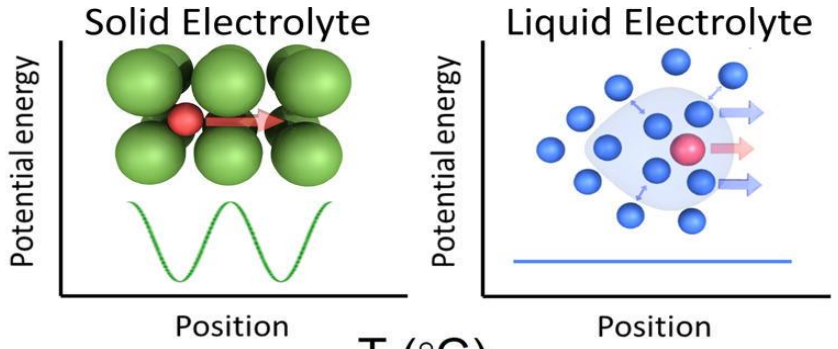
(ceramic or polymer ionic conductor)

- high thermal stability
- operation at high temperatures

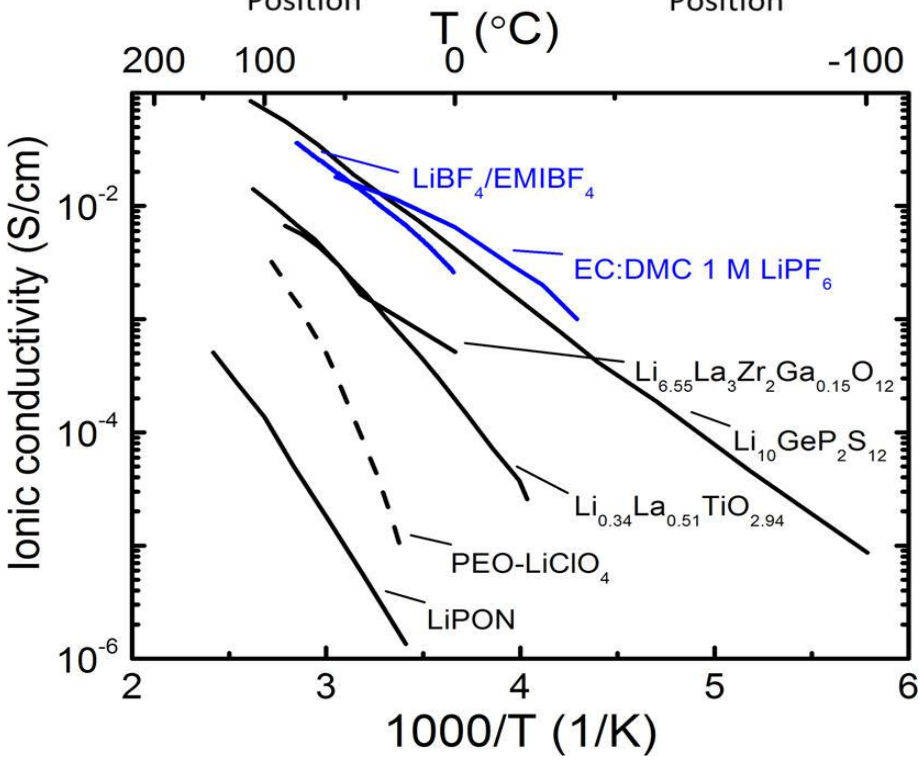
- low ionic conductivity at RT
- increasing conductivity vs T

Solid state electrolytes for Li-ion cells:

interstitial mobile ion
in a crystalline solid

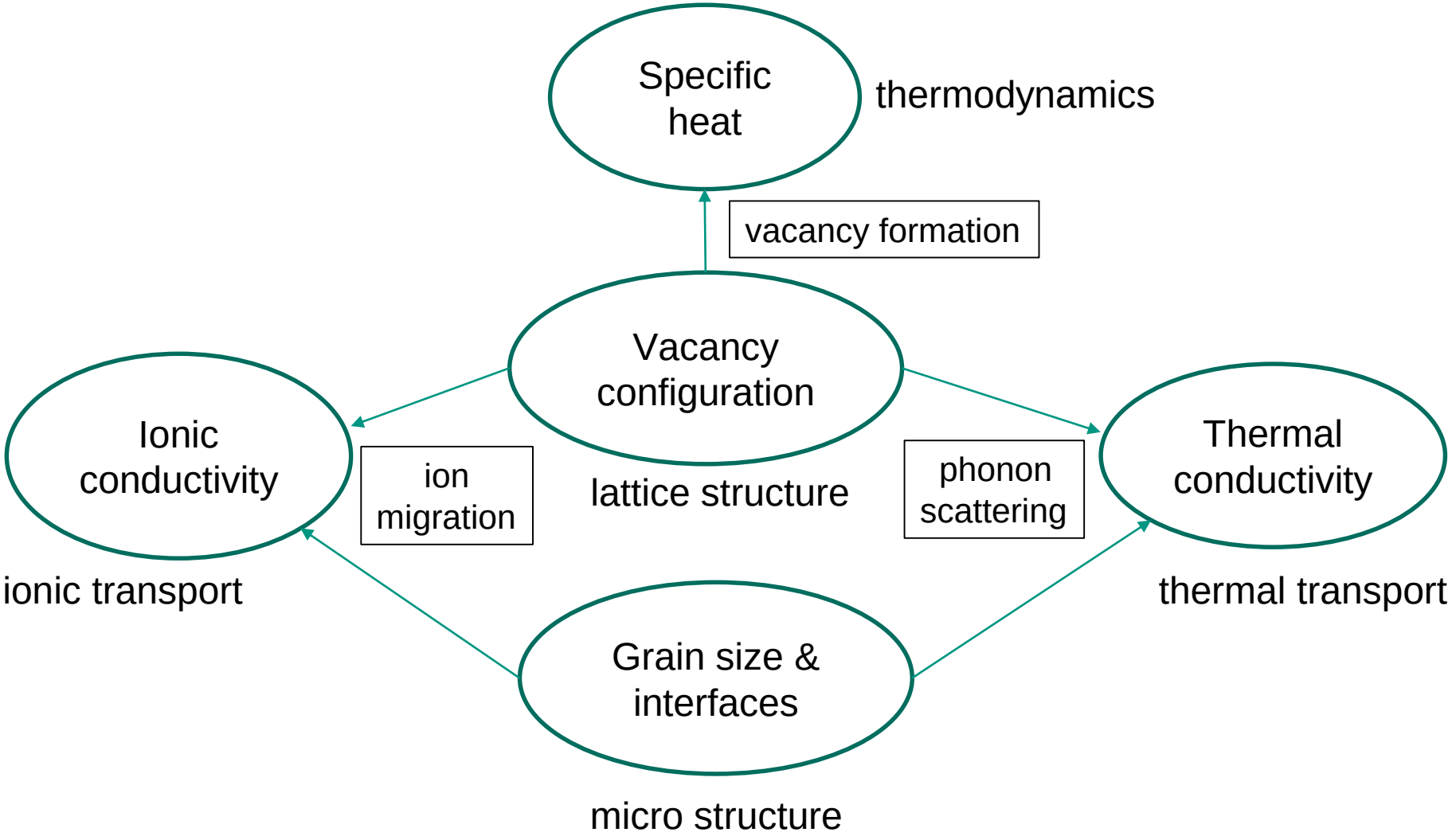


ion within a solvation shell
of electrolyte molecules



J.C. Bachman et. al., Chem. Rev. 2015

Ionic conductors: structure-property relationship



Development for Li-ion and beyond Li

Ceramic NASICON ion conductors: Li^+ → Na^+

***Na**Super**I**onic**CON**ductor*

Ionic conductivity σ_{ion} : medium-high medium-high

Li+ conducting material systems studied:

Li^+-NASICON:	$Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$	Melt quenching, sintering (FAST)
	$Li_{1+x}Al_xGe_{1-x}(PO_4)_3$	Melt quenching, heat treatment (glass route)

Na^+ conducting material systems studied:

Na^+-NASICON:	$Na_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	Commercial powder (NEI Corporation, USA)
	$Na_{1+x}Zr_2(SiO_4)_x(PO_4)_{1-x}$	Synthesis by water based sol-gel route (FZJ)[1]

[1] S. Naquash, Q. Ma, F. Tietz, O. Guillon; Sol. State Ionics 2017

LATP ($Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$) - **Field Assisted Sintering Technology (FAST)**

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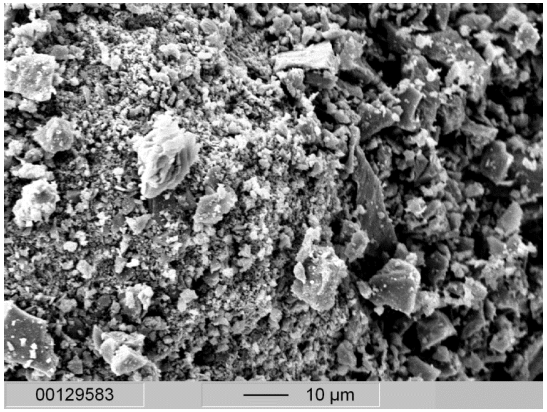
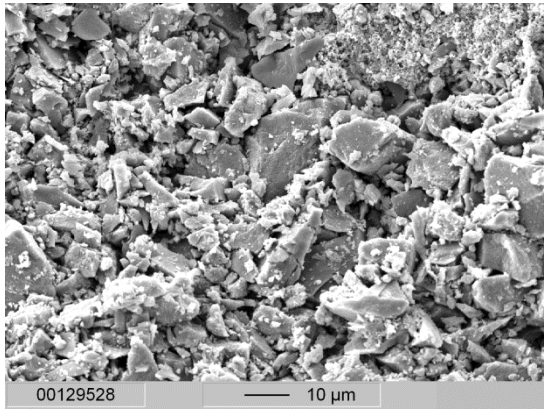
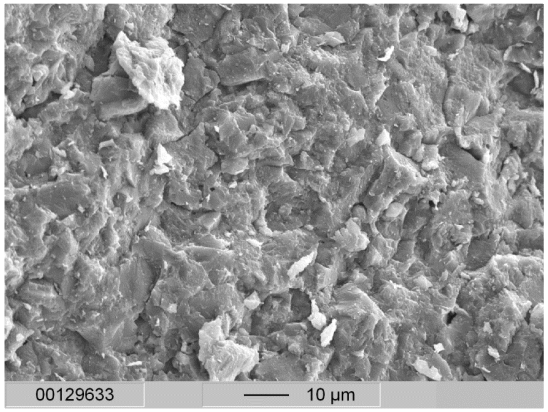
Microstructure



T_S = 600 °C



T_S = 800 °C



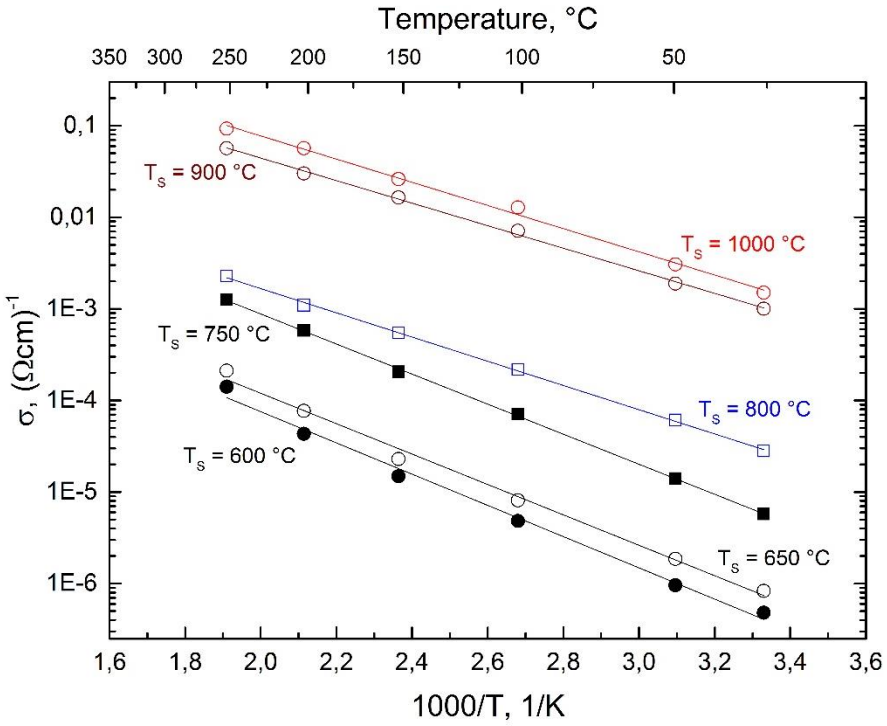
T_S = 1000 °C

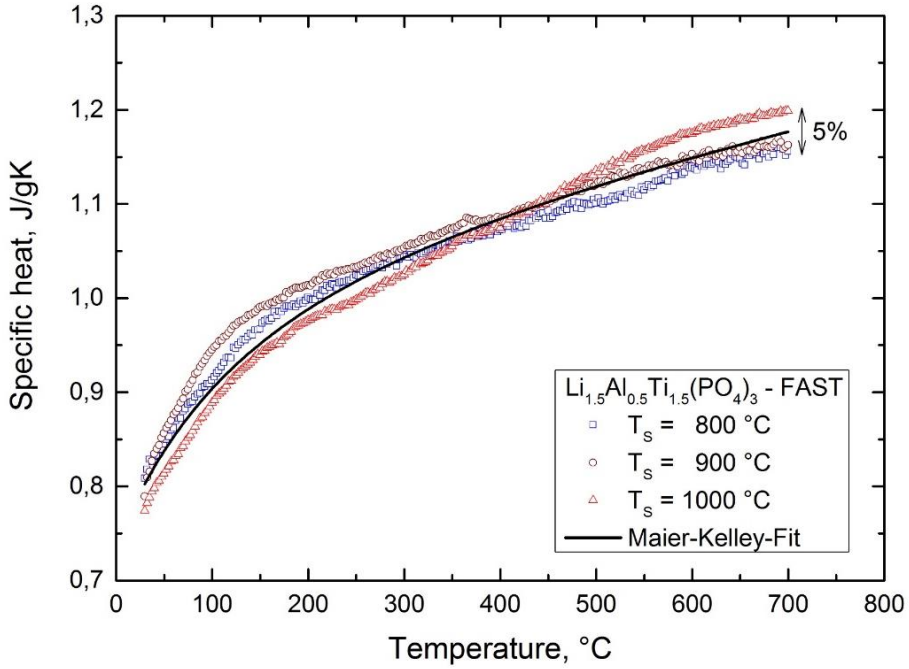
grain growth

increasing density

E. Bucharsky et. al. Ionics (2016)

LATP ($Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$)**: Ionic transport vs. thermodynamics**





Thermally activated conduction:

$$\sigma = A \cdot \exp\left(\frac{-E_a}{k_B \cdot T}\right)$$

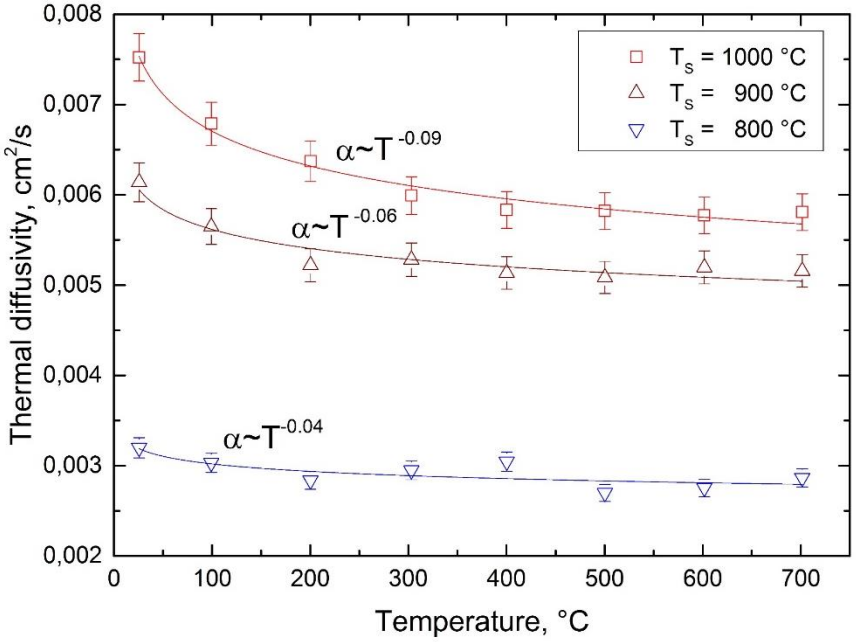
Activation energy: E_a = 0.25 – 0.33 eV

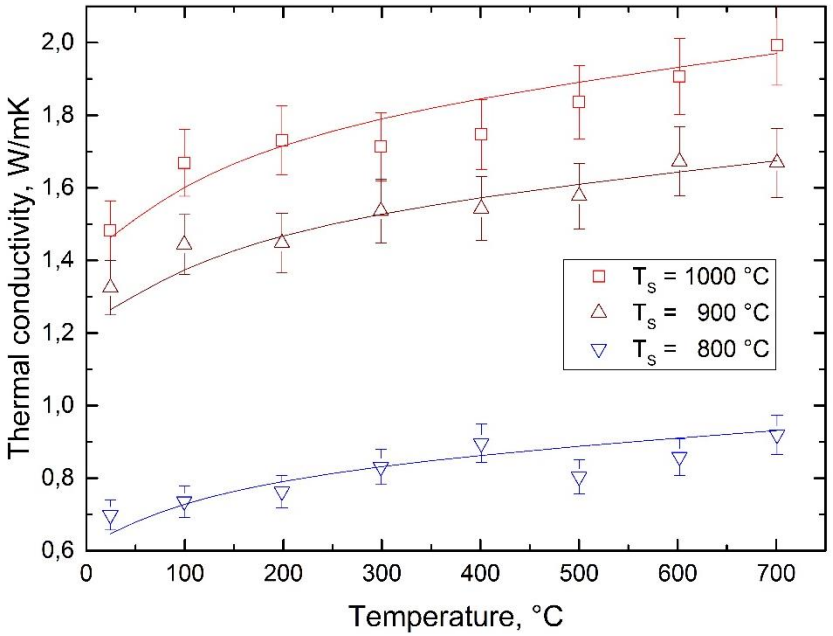
Specific heat can represented by:

$$C_p(T) = A + B \cdot T - C \cdot T^{-2}$$

(Maier-Kelley)

LATP ($Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$)**: Thermal transport properties**





Thermal diffusivity:

- scales with $\alpha \approx T^{-x}$

$$\alpha \propto l_{Phonon}^{-x}$$

- decreases with T_s

Thermal conductivity:

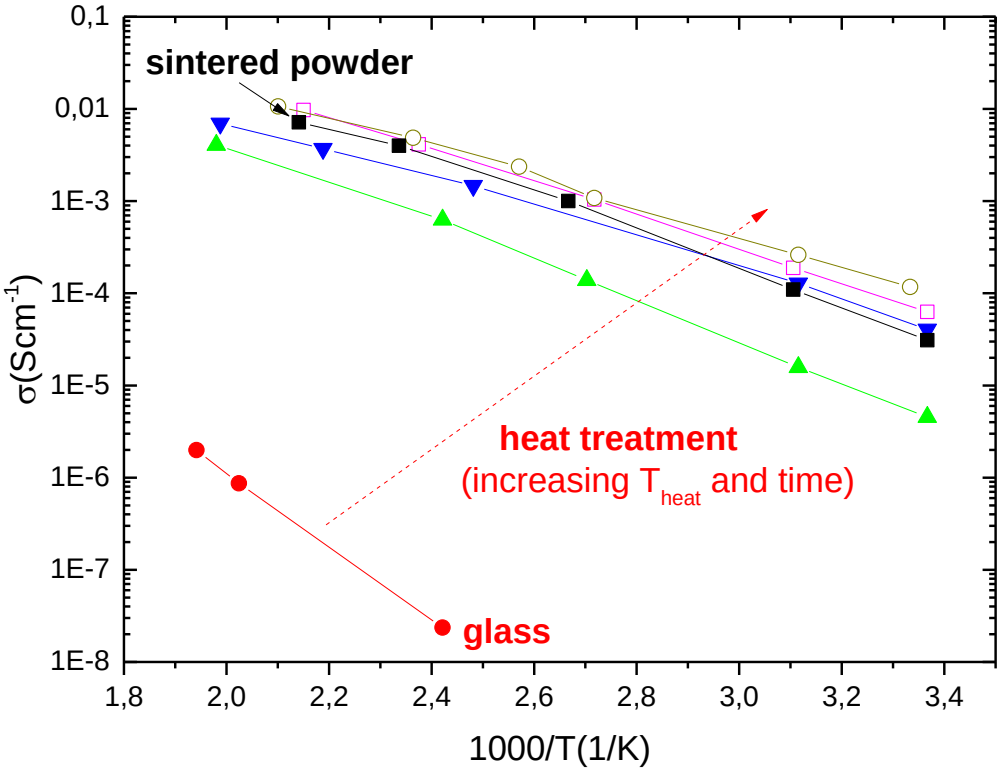
- scales with T_s
- can be described by

$$\lambda \approx \frac{1}{3} \cdot v \cdot c \cdot lPhonon$$

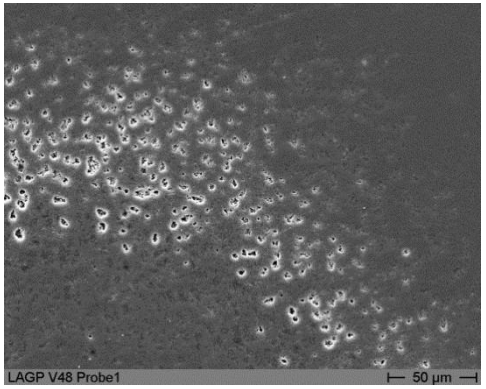
With $\lambda(T) \propto c(T) \cdot l_{Phonon}^{-x}$

LAGP ($Li_{1+x}Al_xGe_{1-x}(PO_4)_3$)**: Effects of heat treatment**

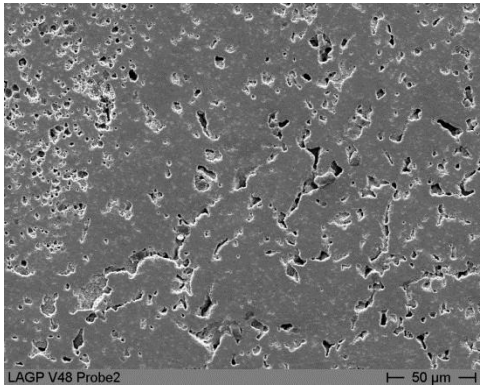
- LAGP: Comparison between powder sintering and glass annealing



Ionic conductivity of LAGP sintered/annealed with different temperatures and duration.



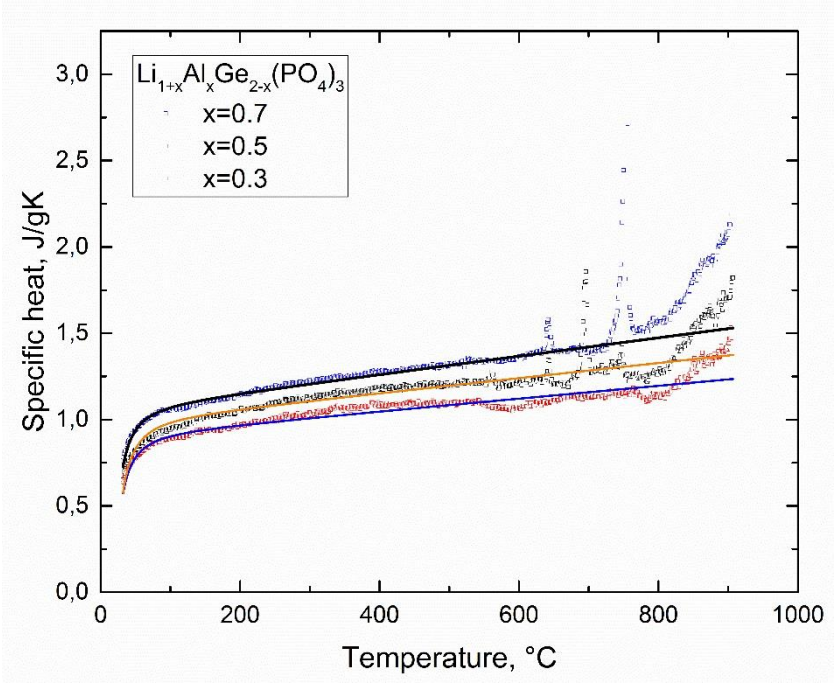
Sample annealed from glass

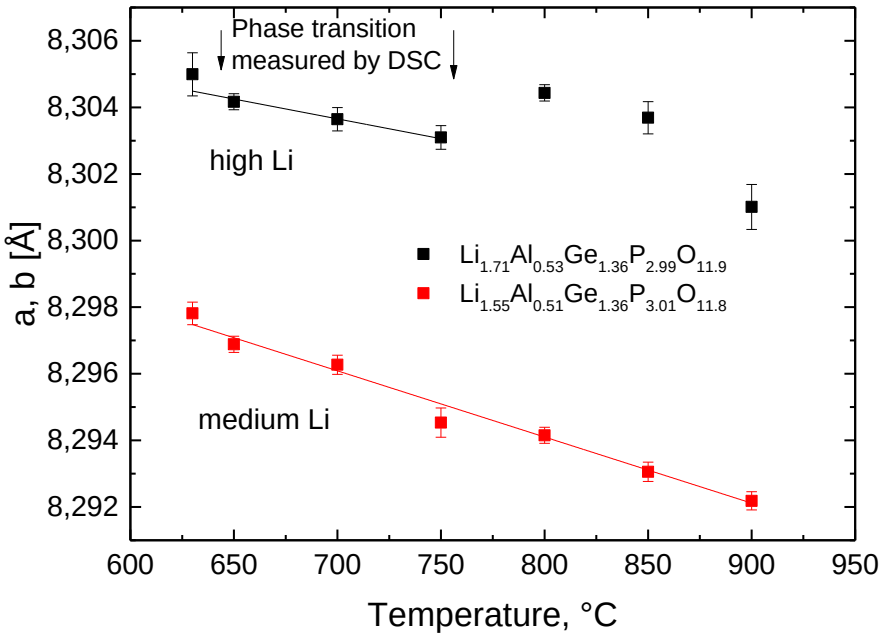


Sample sintered from powder

LAGP ($Li_{1+x}Al_xGe_{1-x}(PO_4)_3$)**: Specific heat and phase transitions**

Increasing lattice distortion: Low Li (x=1.3) ➞ Medium Li (x=1.5) ➞ High Li (x=1.7)





C_p (T)–data: $Li_xAlGe(PO_3)_4$ x= 1.3, 1.5, 1.7

$$C_p(T) = A + B \cdot T - C \cdot T^{-2}$$

(Maier-Kelley)

High temperature XRD:

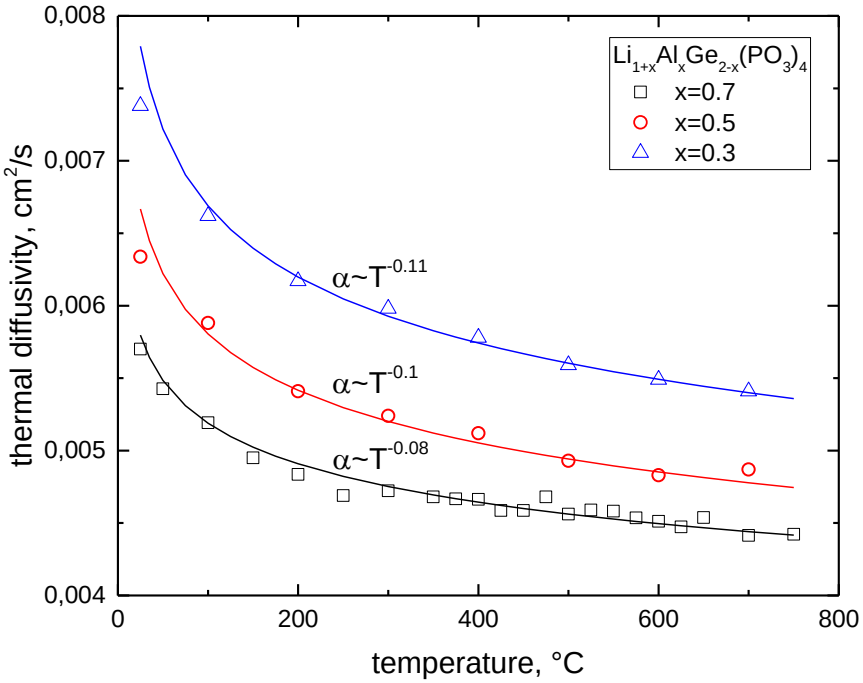
a-, b-axis decreases

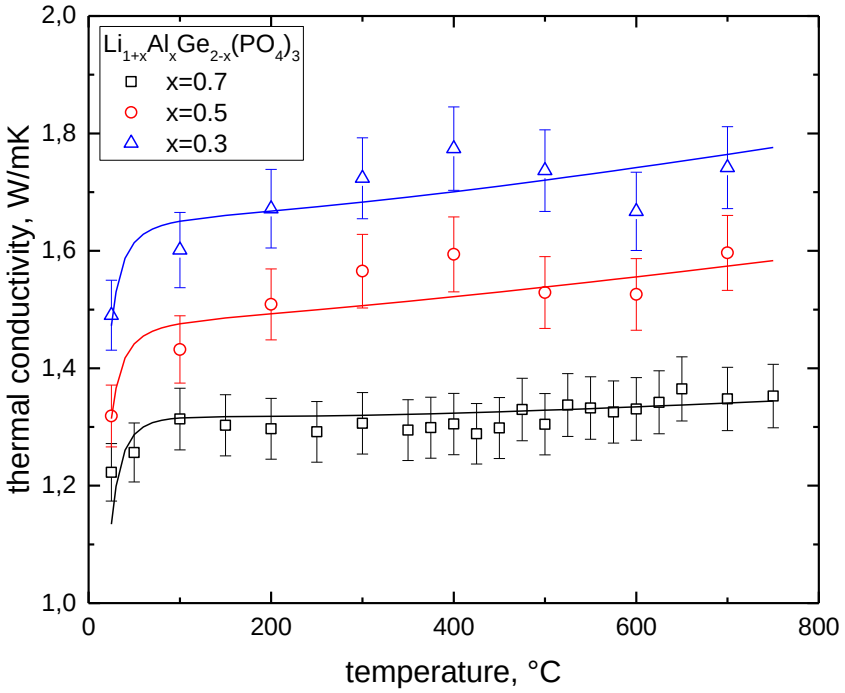
c- axis increases

cell volume expansion vs T

Y. Cui et. al. Solid State Ionics 289 (2016)

LAGP ($Li_{1+x}Al_xGe_{1-x}(PO_4)_3$): **Thermal transport properties**





Thermal diffusivity:

- scales with $\alpha \approx T^{-x}$

$$\alpha \propto l_{Phonon}$$

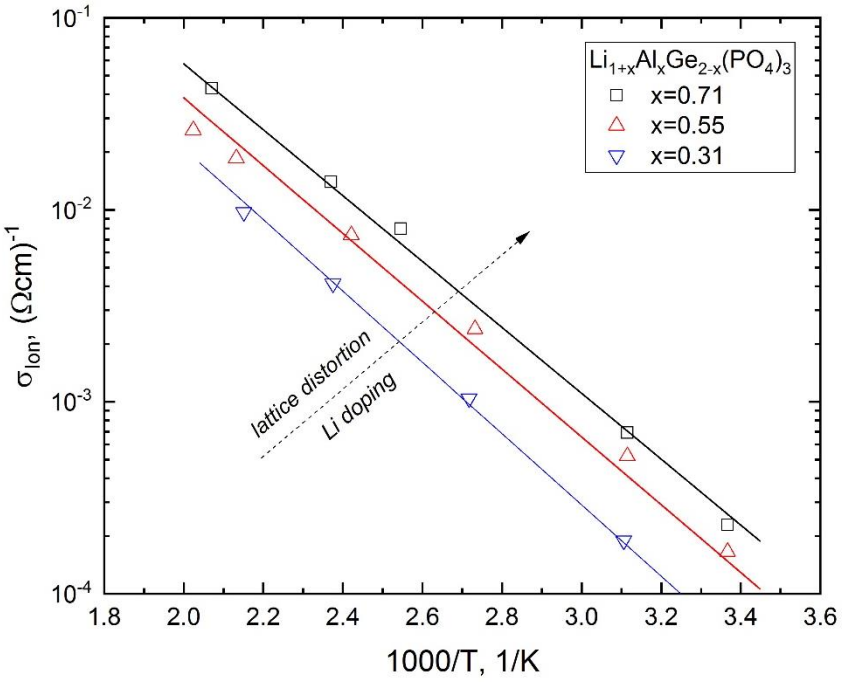
- decreases with doping level

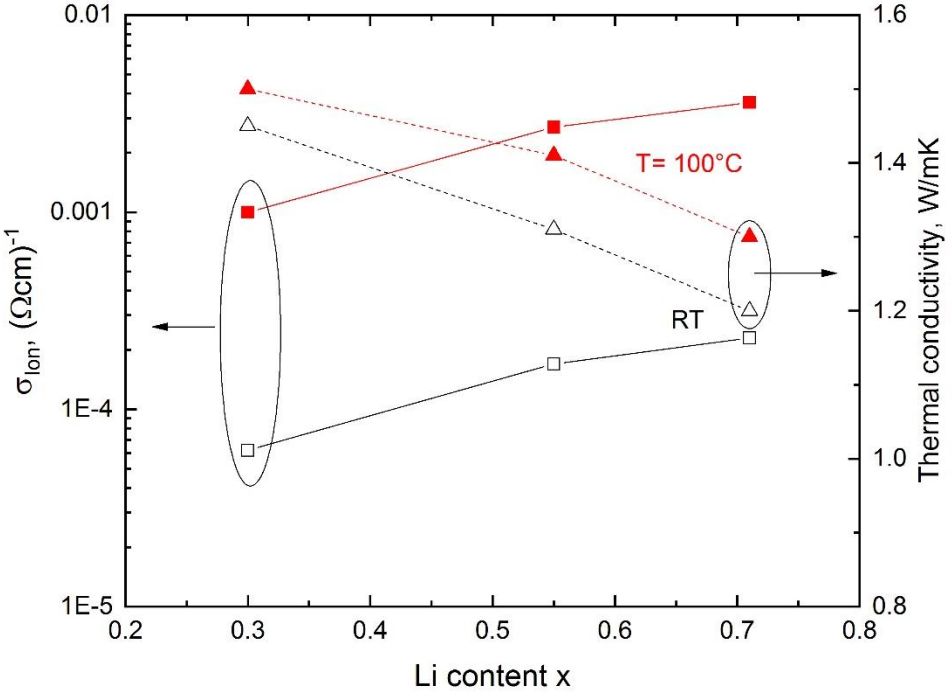
Thermal conductivity:

- weakly dependent on T
- decreases with Li content

$$\lambda \approx \frac{1}{3} \cdot v \cdot c \cdot lPhonon$$

LAGP ($Li_{1+x}Al_xGe_{1-x}(PO_4)_3$)**: Ionic vs. thermal conductivity**





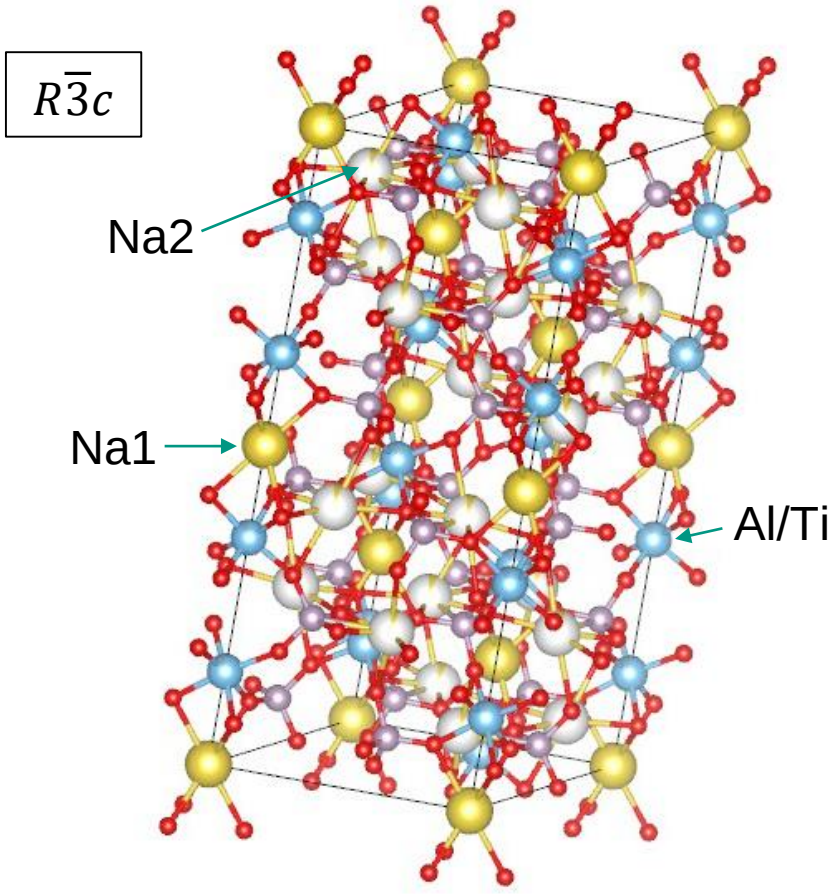
Ionic conductivity:

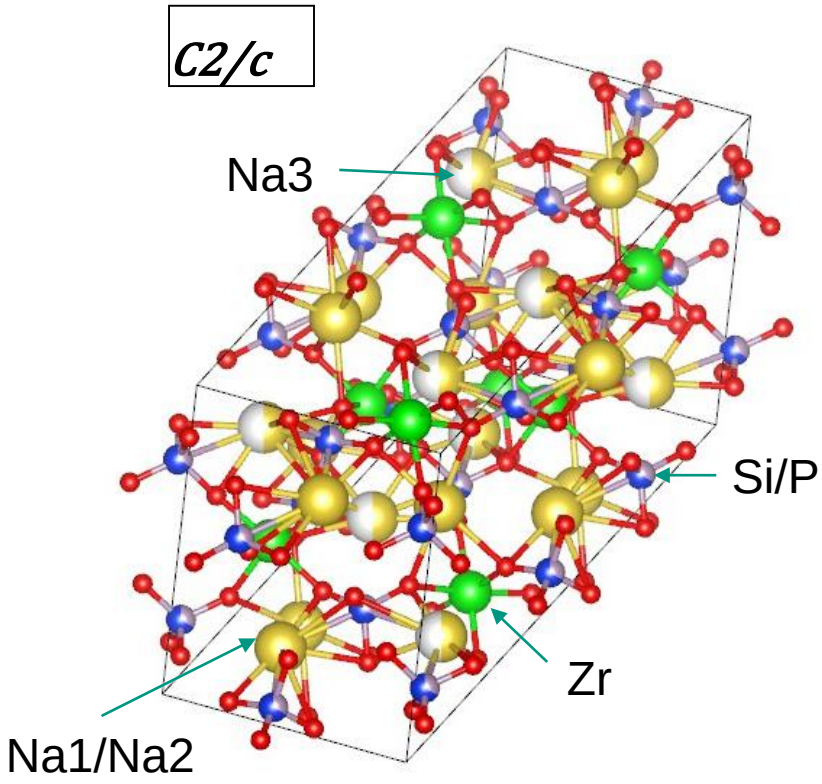
- large variation within $\Delta T \approx 200$ K
- thermally activated: $\sigma = \sigma_0 \cdot e^{-E_a/k_B T}$
- increases with doping level

Thermal conductivity:

- small variation with temperature
- decreases with doping level

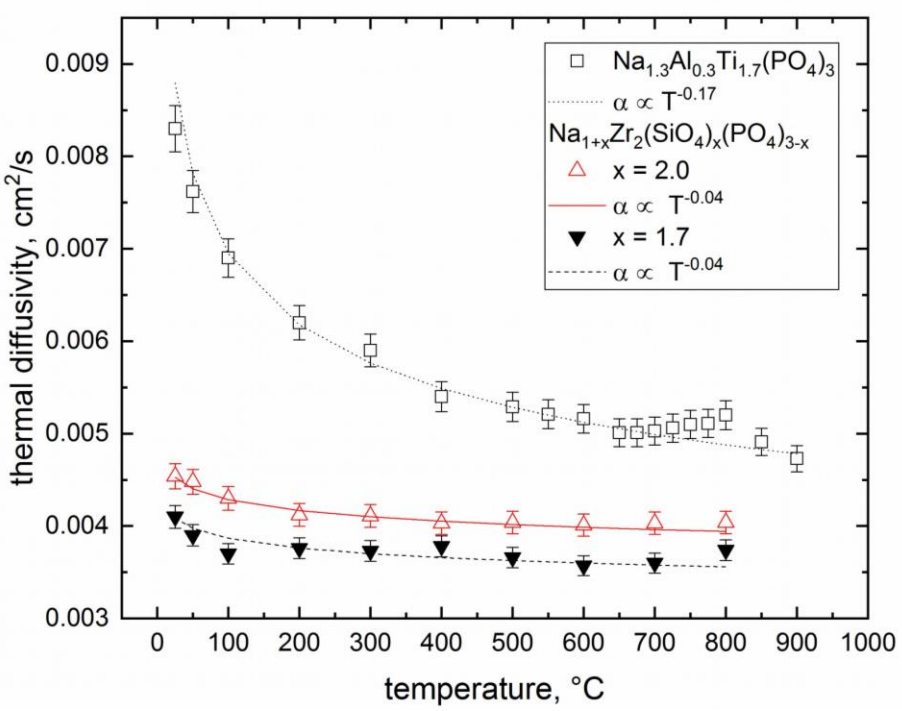
Na^+ conducting NASICON systems

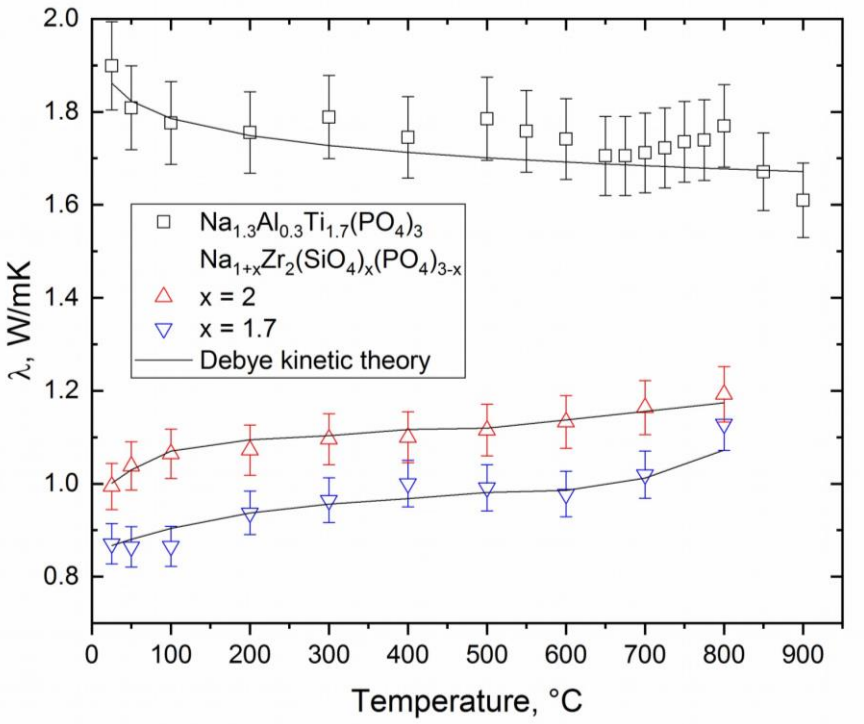




$$Na_{1+x}Al_xTi_{2-x}(PO_4)_3 \xrightarrow[\text{Na doping}]{\text{ion exchange}} Na_3Zr_2(SiO_4)_2(PO_4)$$

NATP and **NaZSiP :** **Thermal transport**





Thermal diffusivity:

- scales with $\alpha \approx T^{-p}$

$\alpha \propto l_{Phonon}$

Thermal conductivity:

- weakly dependent on T

- $\lambda \approx \frac{1}{3} \cdot v \cdot c \cdot l_{Phonon}$

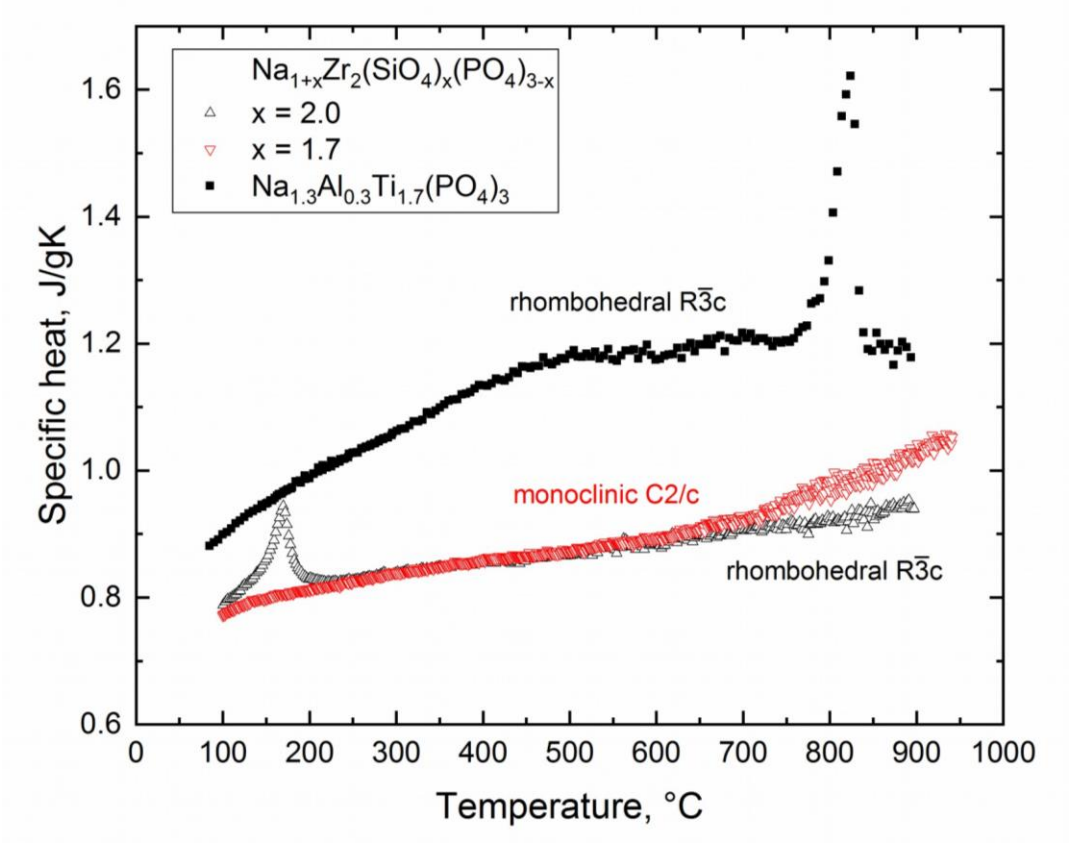
NATP and NaZSiP: Specific heat capacity

NATP:

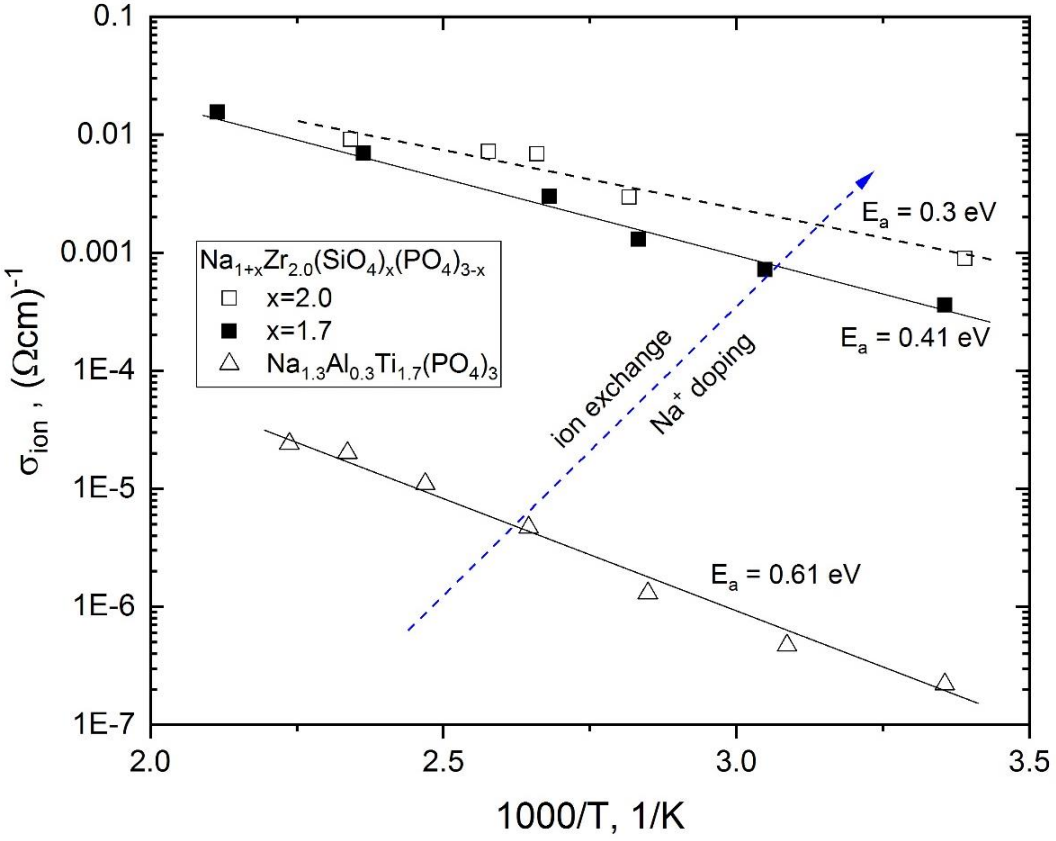
- Cp(T) continuously increasing
- Phase transformation for 700 < T < 800 °C
- Nature of the transformation to be clarified by HT-XRD

NaZSiP:

- Phase transformation in Cp-data for “stoichiometric” $Na_{3.0}ZSiP$
- Strong anharmonic contribution above 800 °C in $Na_{2.7}ZSiP$



NATP and NaZSiP: Ionic conductivity



NaZSiP

$Na_3Zr_2(SiO_4)_2(PO_4)$

$C2/c$

NATP

$Na_{1+x}Al_xTi_{2-x}(PO_4)_3$

$R\bar{3}c$

σ_{ion} increases and activation energy E_a decreases by Na^+ doping

Summary

Ceramic materials for solid electrolytes:

- Li^+ / Na^+ conducting NASICON model systems

- Thermally activated ionic conduction depends on doping and structure

- Increasing ion conduction ⟶ decreasing thermal conductivity / diffusivity

- Phonon mean free path comparable with hopping distance

- Specific heat $c_p(T)$ data open access to thermodynamic data and modeling

Acknowledgement

Na^+ conducting systems:
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Li^+ conducting systems:
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