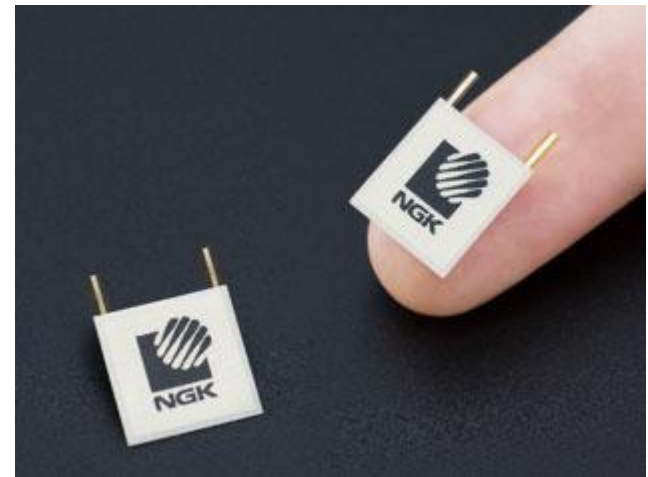
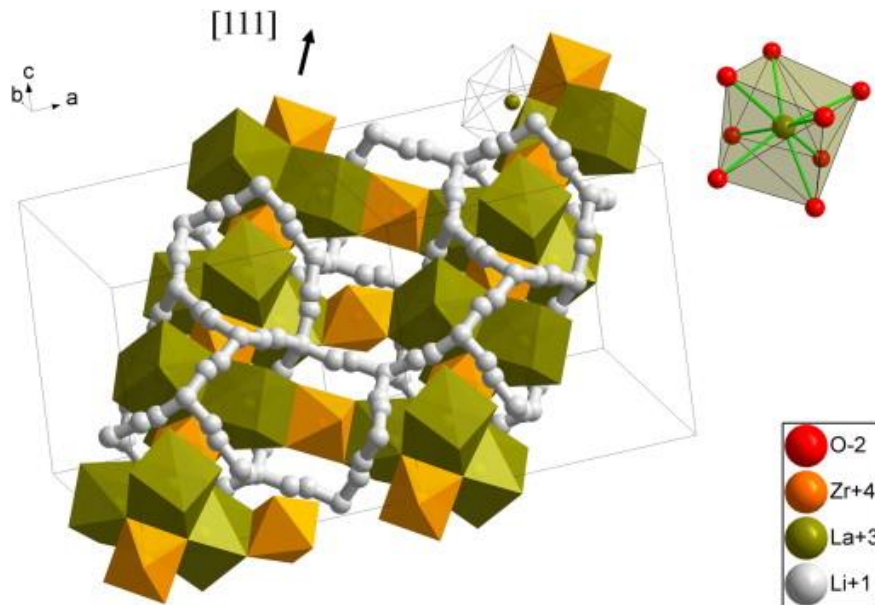


# Fast Li<sup>+</sup> ion conducting garnets

The key to safe and compact energy storage?



[www.ngk.co.jp](http://www.ngk.co.jp)

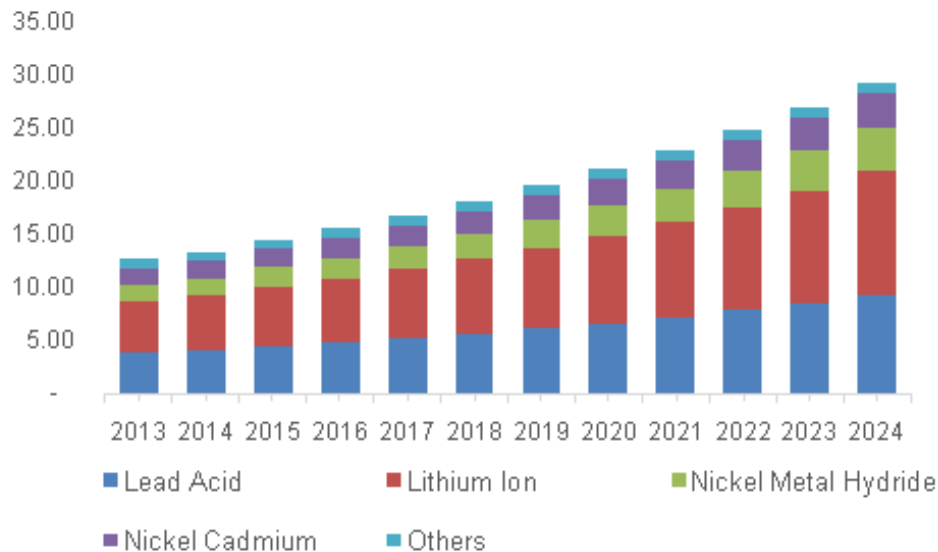
Michael Rawlence – [michael.rawlence@empa.ch](mailto:michael.rawlence@empa.ch)

# Contents

- The Battery Market
- Basic Principles of Batteries
- Current Lithium ion battery limitations
- Introducing Solid State Lithium Ion Batteries
- Current Progress
- Recent work
- Conclusion

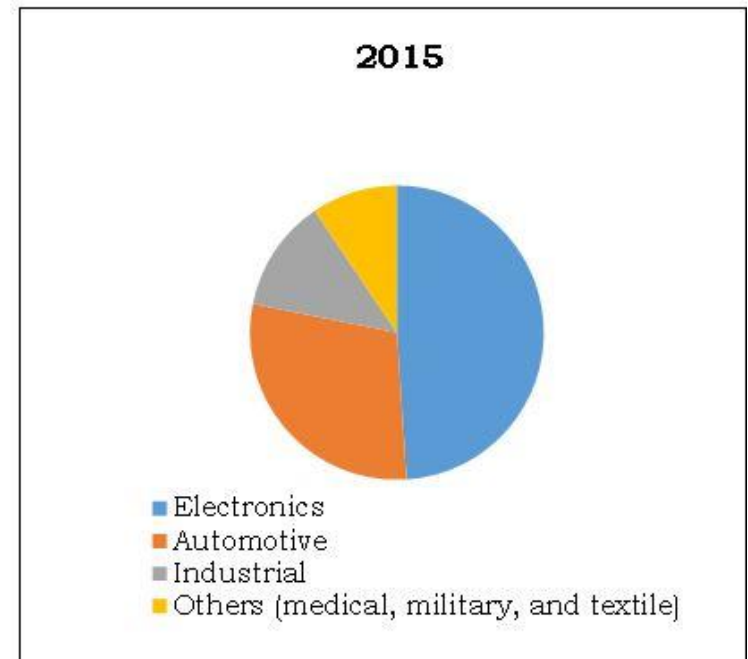
# The Battery Market

North America battery market revenue by product, 2013 - 2024 (USD Million)



Grand View Research, Industry Analysis 2016

Global Lithium-ion Battery Market Share by Industry



Allied Market Research, Lithium-Ion Battery Market Overview 2016

# Why is Lithium-ion Leading?

## Lead Acid

- Economical
- High tolerance (mechanical and thermal)
- Low energy density

## Nickel Cadmium

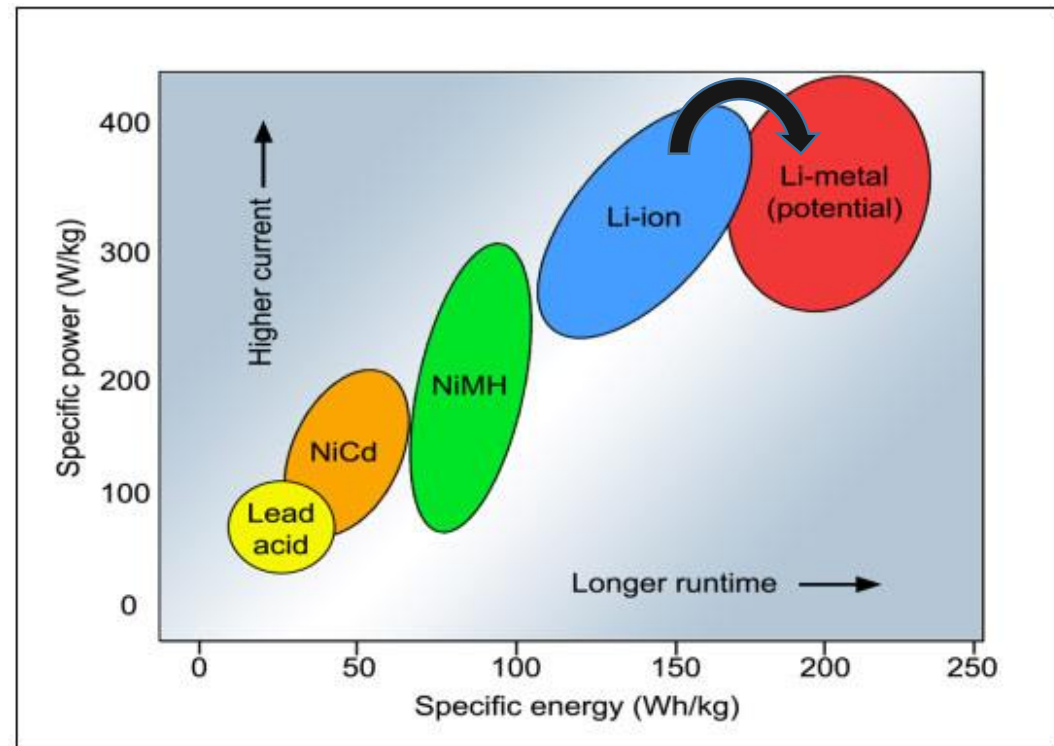
- Long lifetime (1500 cycles)
- High power
- Low energy density

## Nickel-Metal Hydride

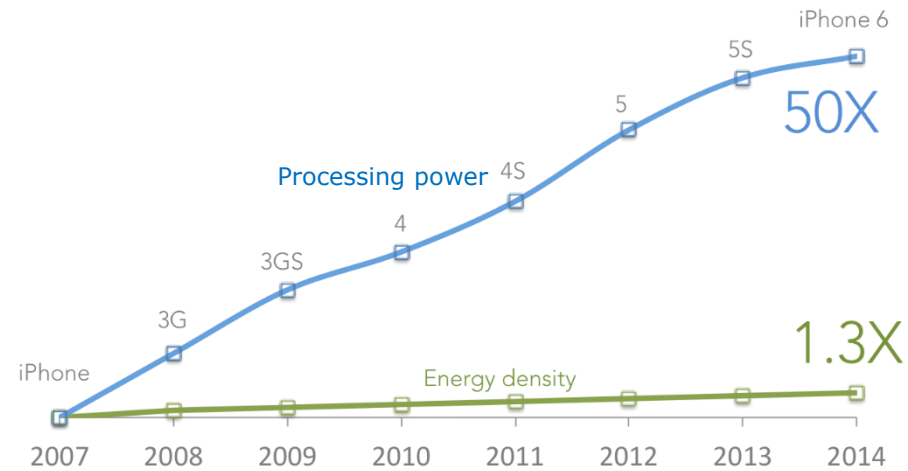
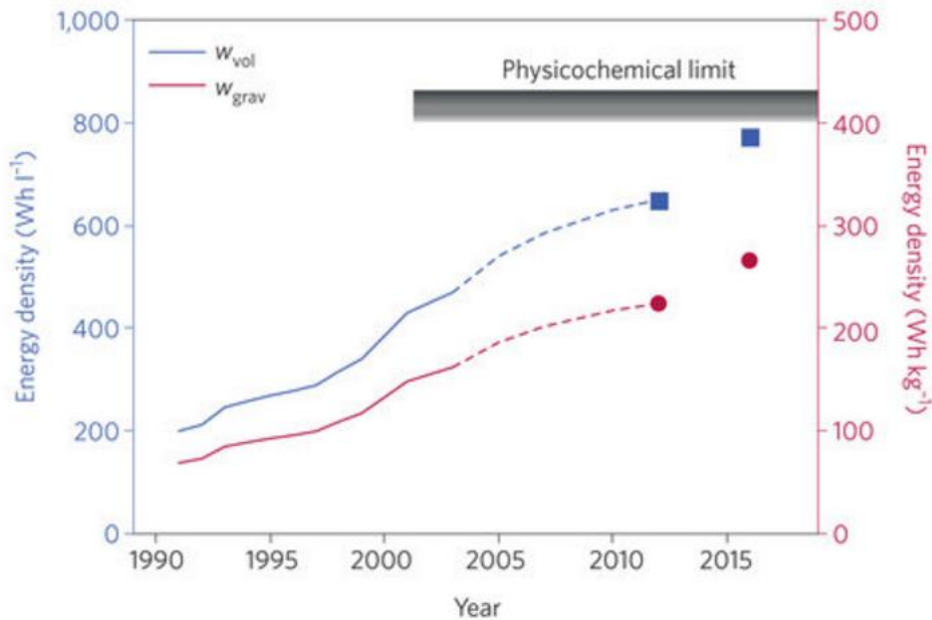
- Higher energy density
- Environmentally friendly
- High self-discharge

## Lithium-ion

- High energy density
- Good lifetime (<1000 cycles)
- Expensive

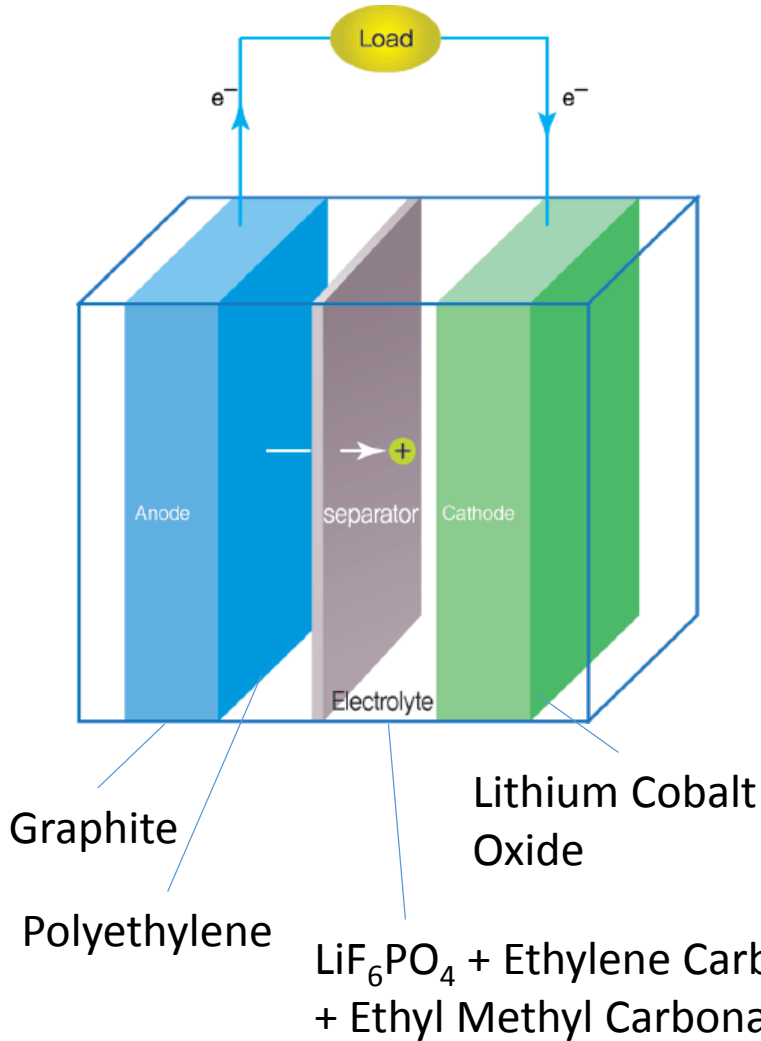


# Approaching the Limit?

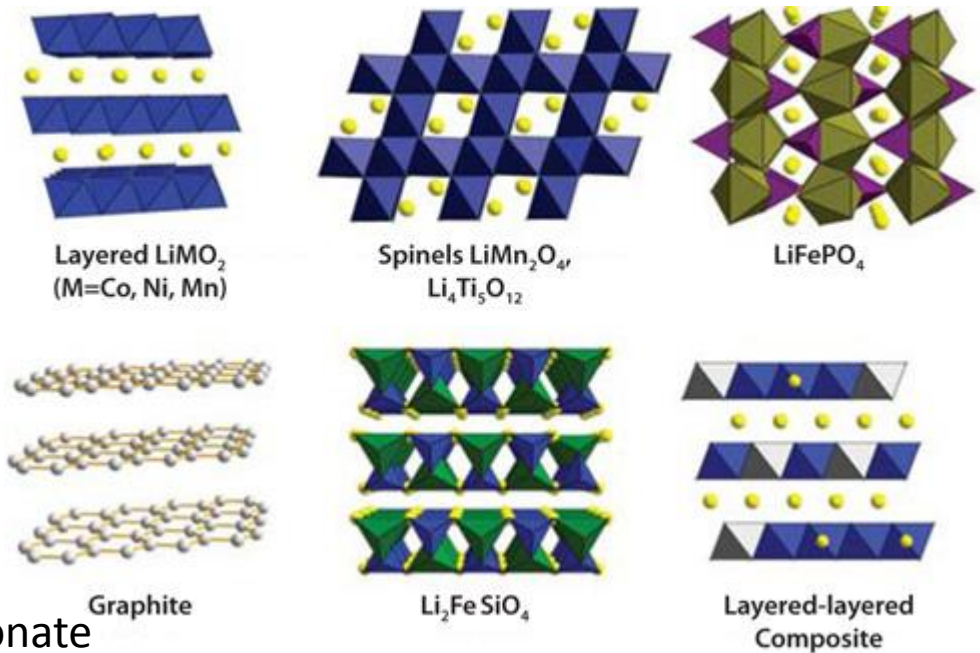


Janek, Jürgen, and Wolfgang G. Zeier. *Nature Energy* 1 (September 8, 2016): 16141.

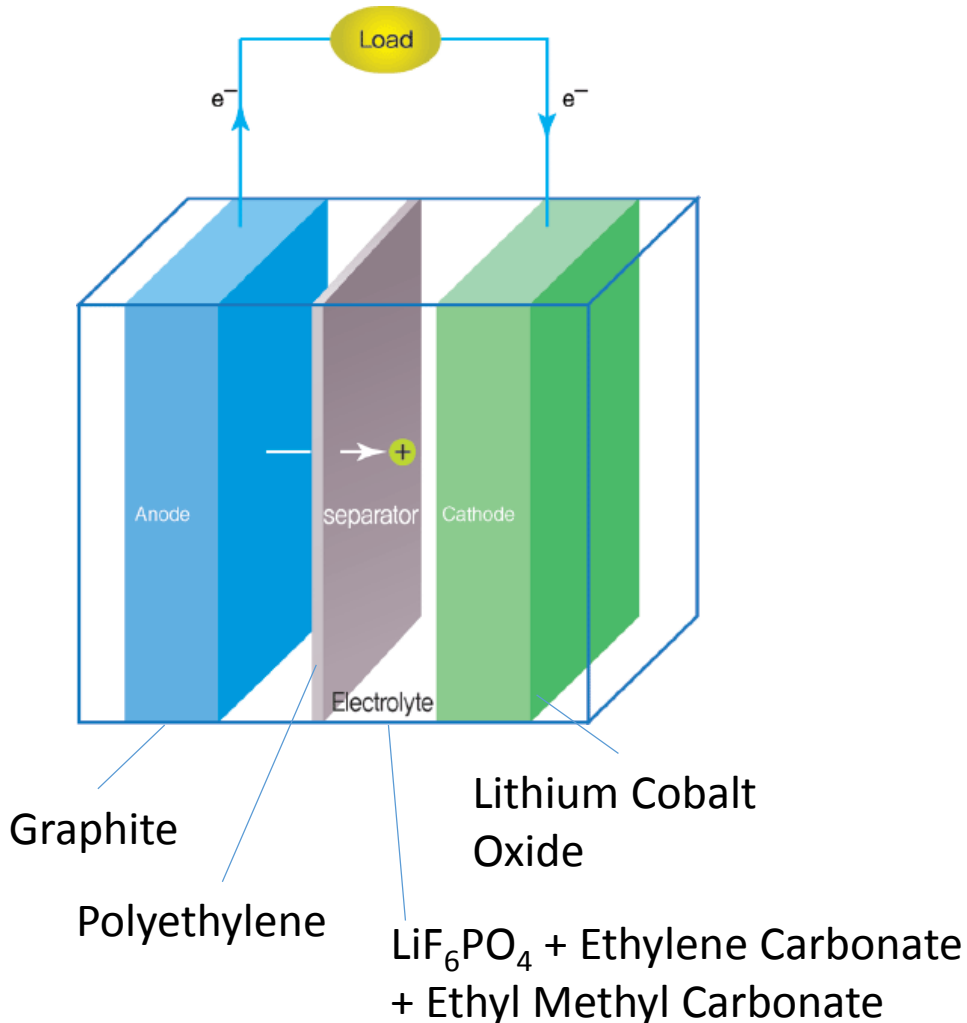
# Battery Basics



- Electrode choice determines:
- Charge
  - Voltage
  - Optimum Current
  - Max Lifetime



# Battery Basics



$\text{LiCoO}_2$ :

Nominal voltage of 3.8V vs. Li

140 mAh/g

Maximum discharge rate of 1C  
500-1000 cycles

Cobalt is expensive

Graphite:

0.1 – 0.3V vs. Li

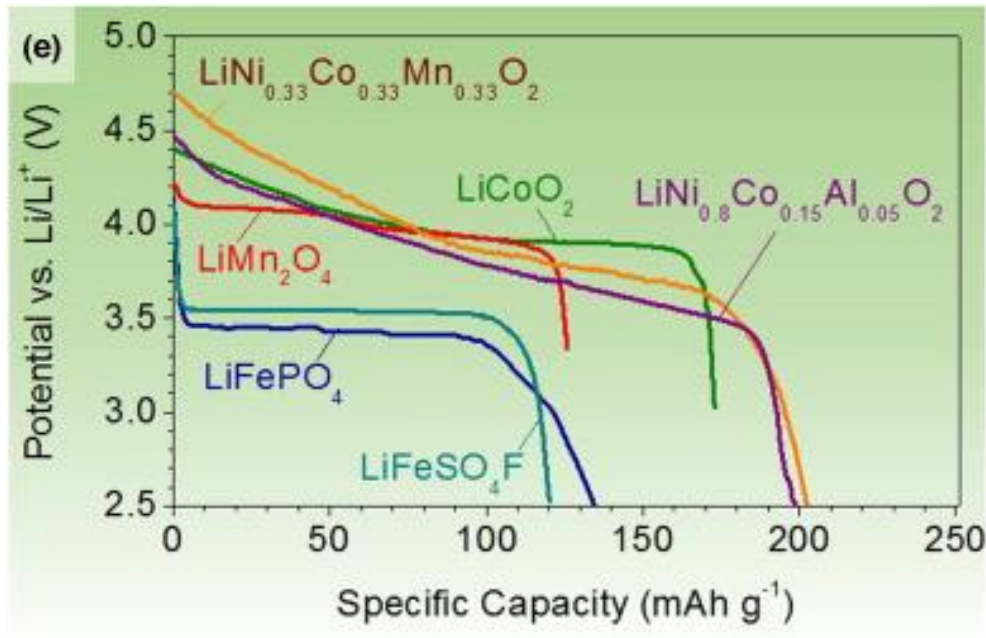
372 mAh/g

Long Cycle life >1500

Calendar life reduction due to reactions with liquid electrolyte

# Battery Basics

## Galvanostatic Measurement



Ideal Anode?

Lithium Metal:

Capacity 3860 mAh/g

0 V vs. Lithium (surprise)



# Limitations of current Li-ion cells

Low cathode capacities. Best practical capacity to date:

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  with 200 mAh/g

Reactions with electrolyte occur above 4V.

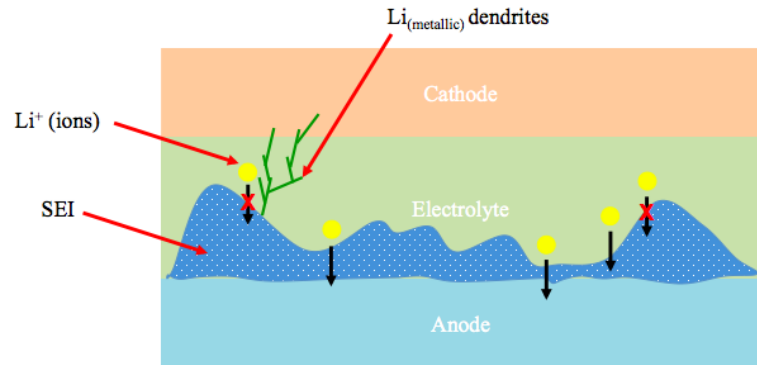
Reactions with electrolyte and dendrite growth occur at high charge rates (or when using metallic lithium).

Bulky encapsulation required to prevent electrolyte leakages

Lifetime ultimately limited by parasitic reactions with electrolyte over time.

# Limitations of current Li-ion cells

- Dendrite Formation



=



# Better Batteries Mean...



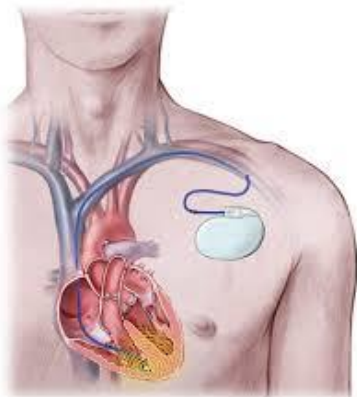
**Connect Wider**



**Drive Faster**



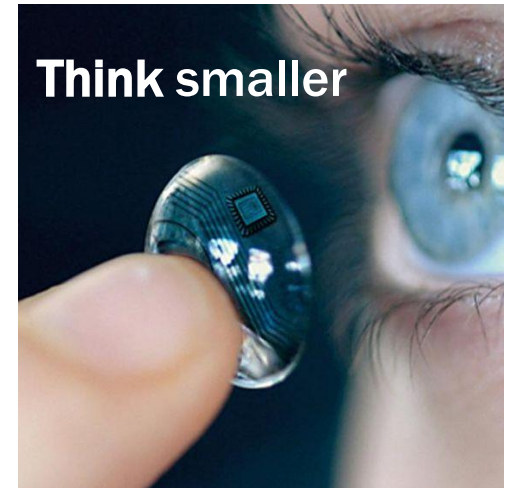
**Fly Higher**



**Live Safer**



**Last Longer**



**Think smaller**

# Solid State Li-ion Batteries

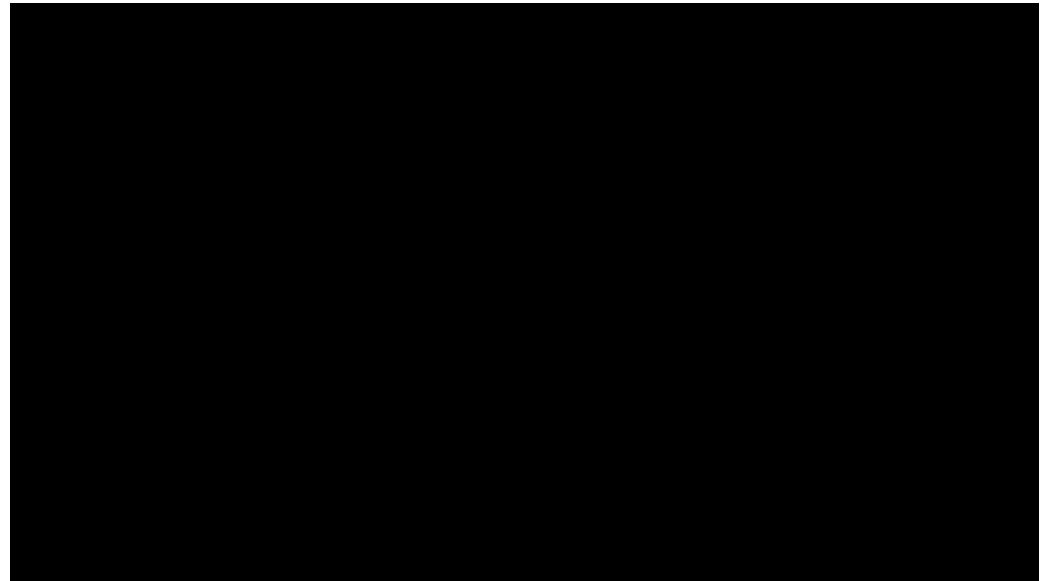
No risk of leakages

No flammable materials

Less reactive to electrodes

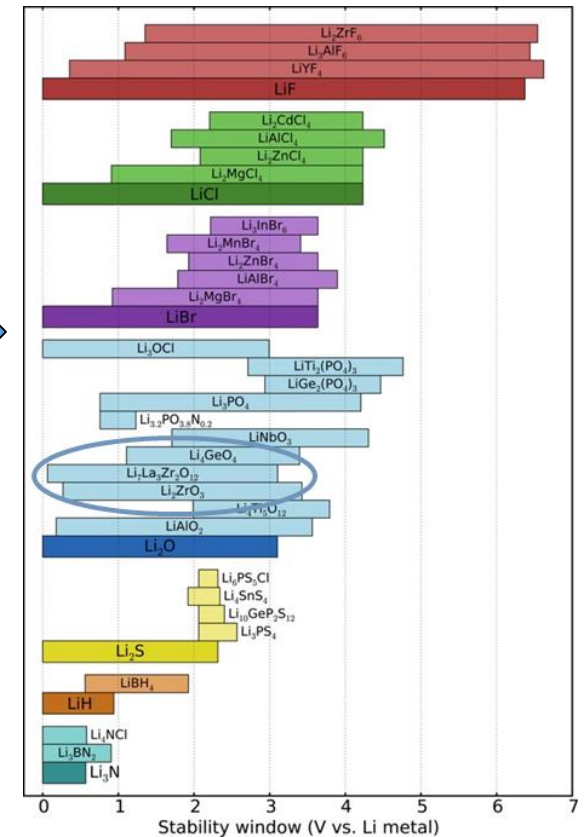
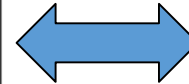
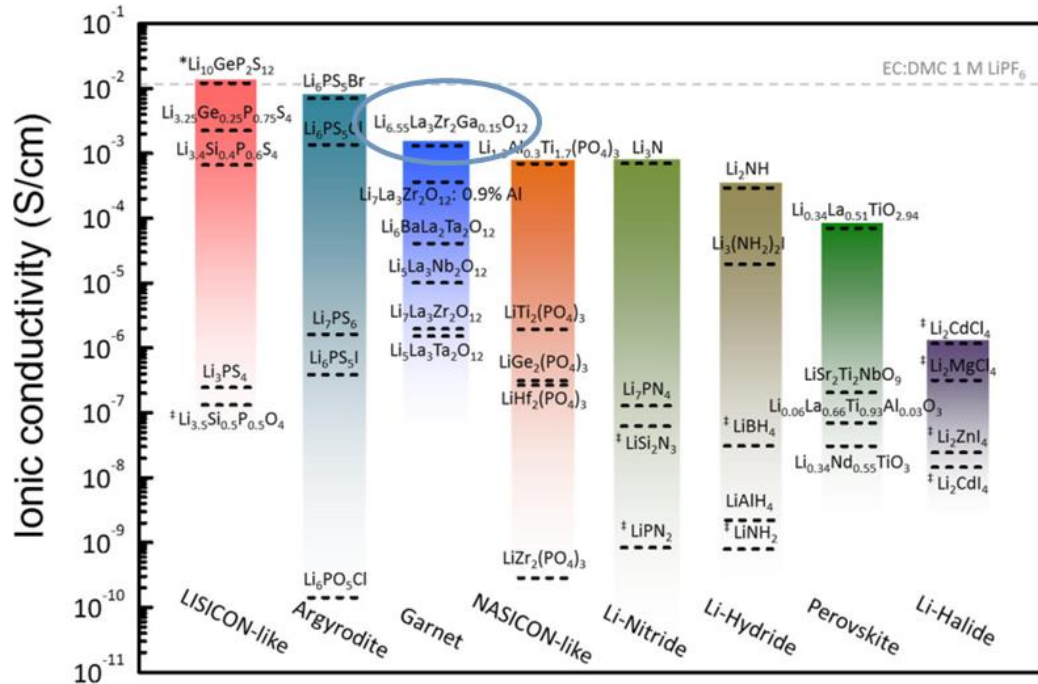
- ↑ Voltage
- ↑ Rate
- ↑ Lifetime

Higher tolerance to temperature  
(performs better when hot)



Kato, Yuki, Satoshi Hori, Toshiya Saito, Kota Suzuki, Masaaki Hirayama, Akio Mitsui, Masao Yonemura, Hideki Iba, and Ryoji Kanno. *Nature Energy* 1, no. 4 (2016): 16030

# Introducing Solid State Electrolytes



**Garnet solid state electrolyte:  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$**

- ❖ **High Li-ion conductivity** (bulk, doped).
- ❖ **Wide theoretical electrochemical stability window** (larger in practice).
- ❖ **Stable against Li-metal.**
- ❖ **Crystallization temperature below 700 °C** reported.

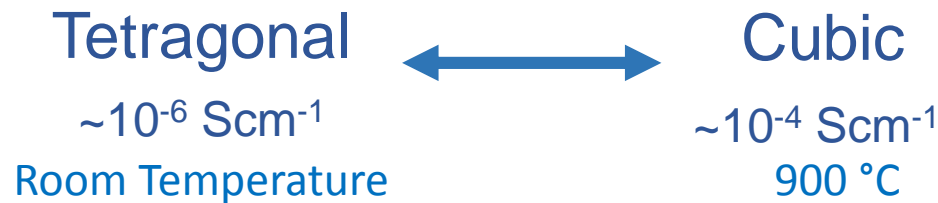
J. C. Bachman et al, Chem. Rev. 2016, 116, 140.

W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim, G. Ceder, Chem. Mater. 2016, 28, 266.

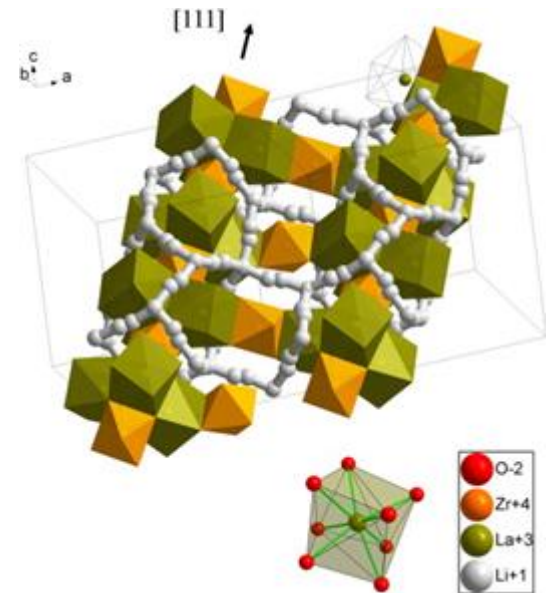
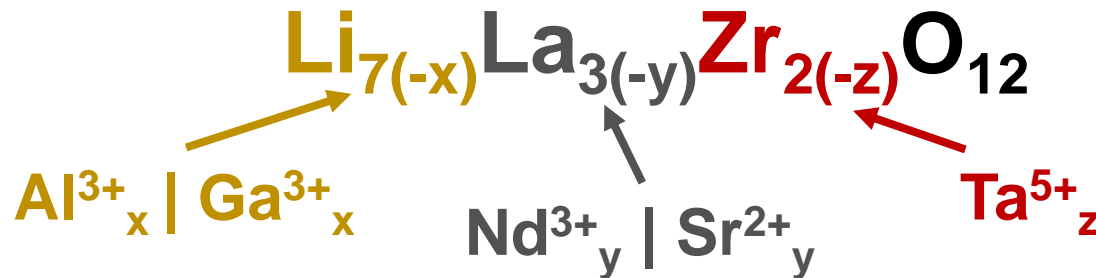
# Phases of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)

## Crystal structure stabilization for maximizing $\text{Li}^+$ conductivity

High  $\text{Li}^+$  mobility **dependent on crystal structure**



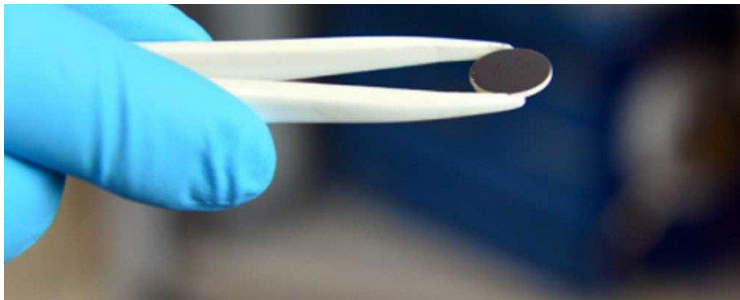
Cubic garnet phase stabilization by **doping**:



Dumon, A., Huang, M., Shen, Y., and Nan, C. W. (2013). *Solid State Ionics* 243, 36–41

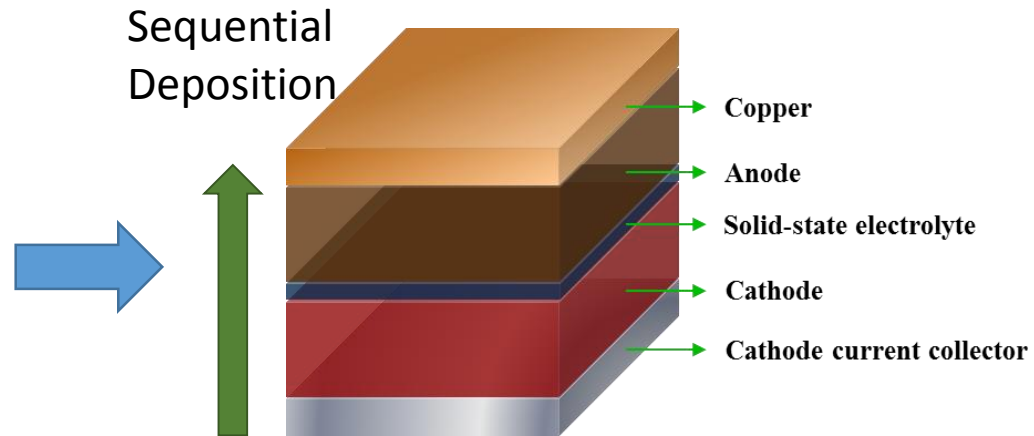
# Battery Integration

Bulk Pellet



Electrolyte 200  $\mu\text{m}$   
Cathode 5  $\mu\text{m}$

Thin Film



Electrolyte 0.2  $\mu\text{m}$   
Cathode 5  $\mu\text{m}$

# Thin Film Deposition

Method	Phases	Morphology	Substrate	Li-ion Conductivity (RT)
PLD <sup>1</sup>	c-LLZO, t-LLZO, LZO	Unmeasured	MgO	$1.6 \times 10^{-6} \text{ Scm}^{-1}$
PLD <sup>2</sup>	c-LLZO	Cracked	SrTiO <sub>3</sub>	$3.35 \times 10^{-7} \text{ Scm}^{-1}$
Sputtering <sup>3</sup>	Amorphous	Dense	Stainless steel	$4 \times 10^{-7} \text{ Scm}^{-1}$
Sol-gel <sup>4</sup>	c-LLZO	Porous	MgO	$2.4 \times 10^{-6} \text{ Scm}^{-1}$
Sol-gel <sup>5</sup>	Amorphous, LZO	Porous	SiO <sub>2</sub> /Ti/Pt	$1.6 \times 10^{-6} \text{ Scm}^{-1}$
Aerosol <sup>6</sup>	c-LLZO	Dense	LiFePO <sub>4</sub>	(140°C) $1 \times 10^{-8} \text{ Scm}^{-1}$
MOCVD <sup>7</sup>	c-LLZO	Dense	Poly-Al <sub>2</sub> O <sub>3</sub>	Not measured

Li-ion conductivities of thin films at least X100 lower than bulk pellets!

(1) Park, J. S.; Cheng, L.; Zorba, V.; Mehta, A.; Cabana, J.; Chen, G. Y.; Doeff, M. M.; Richardson, T. J.; Park, J. H.; Son, J. W.; Hong, W. S. *Thin Solid Films* **2015**, 576, 55.

(2) Tan, J. J.; Tiwari, A. *Ecs Solid State Letters* **2012**, 1, Q57.

(3) Kalita, D. J.; Lee, S. H.; Lee, K. S.; Ko, D. H.; Yoon, Y. S. *Solid State Ionics* **2012**, 229, 14.

(4) Tadanaga, K.; Egawa, H.; Hayashi, A.; Tatsumisago, M.; Mosa, J.; Aparicio, M.; Duran, A. *Journal of Power Sources* **2015**, 273, 844.

(5) Chen, R.-J.; Huang, M.; Huang, W.-Z.; Shen, Y.; Lin, Y.-H.; Nan, C.-W. *Journal of Materials Chemistry A* **2014**, 2, 13277.

(6) Ahn, C. W.; Choi, J. J.; Ryu, J.; Hahn, B. D.; Kim, J. W.; Yoon, W. H.; Choi, J. H.; Park, D. S. *Journal of the Electrochemical Society* **2015**, 162, A60.

(7) Katsui, H.; Goto, T. *Thin Solid Films* **2015**, 584, 130.



# Research Goals

- To gain a greater understanding of the crystallization process during thermal treatment.
- Understand the effect of gallium doping on crystallization.
- Form an impurity free thin film with good lithium ion conductivity.

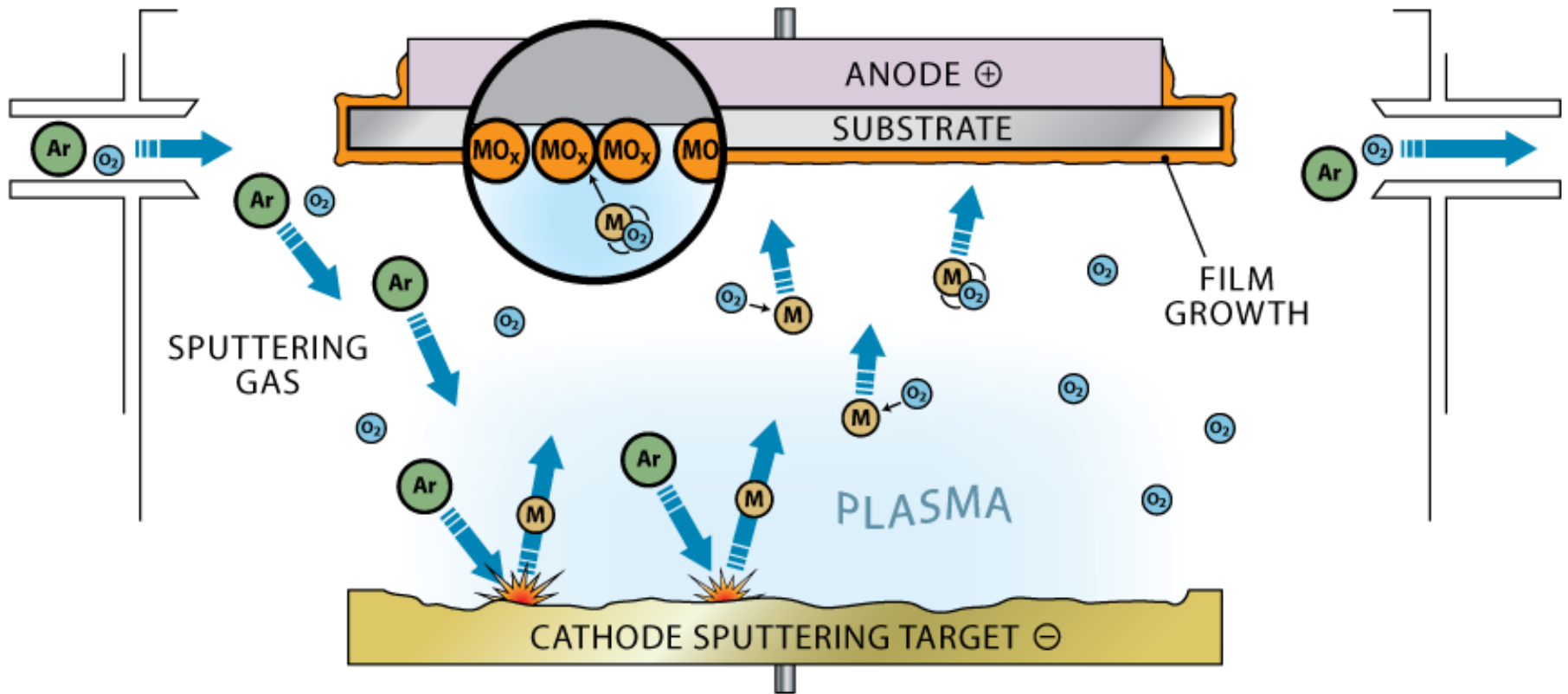
# Sputtering

- 5 target materials
- 3 gas inlets
- Live plasma measurement
- Deposition rate measurement
- Max substrate size 7cm<sup>2</sup>
- Low base pressure ( $1 \times 10^{-8}$  mTorr)

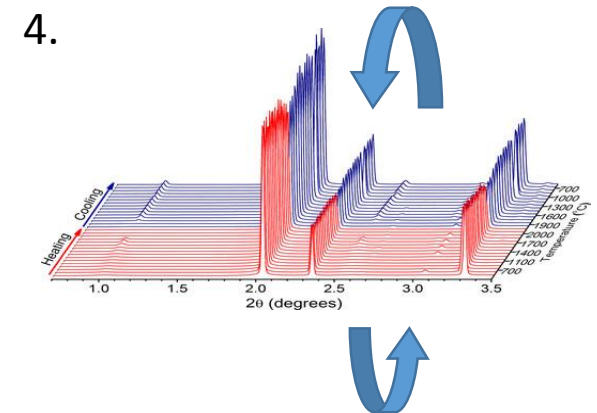
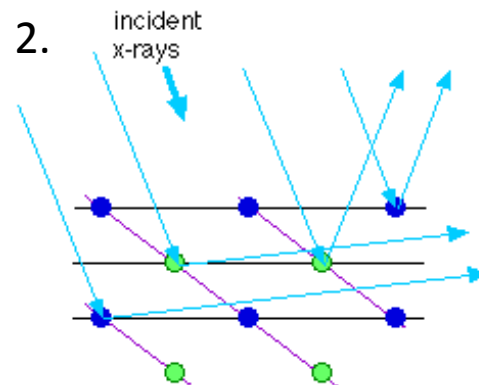
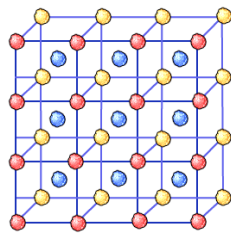
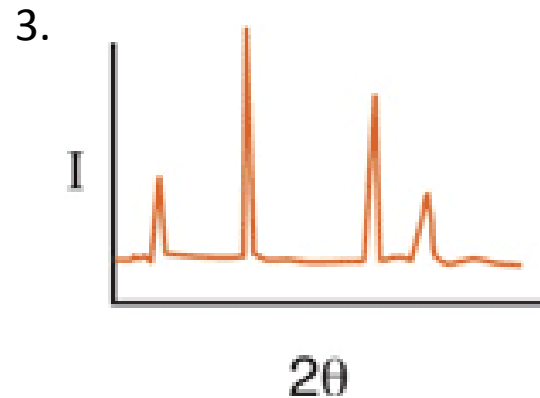
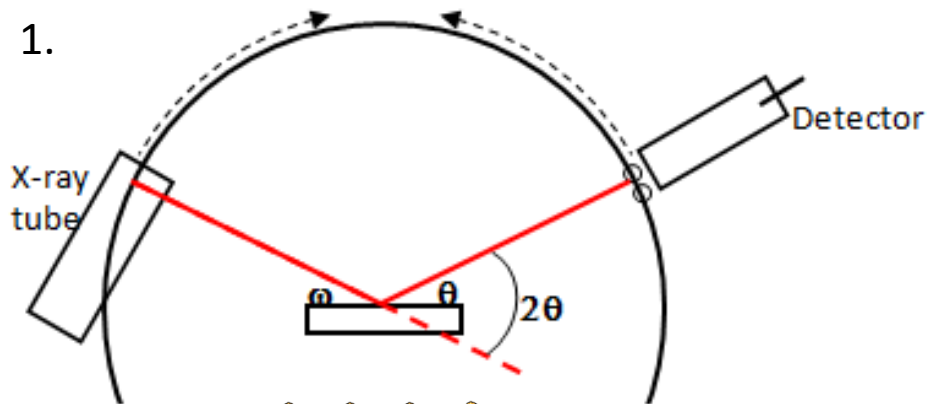


**ORION sputtering deposition system**

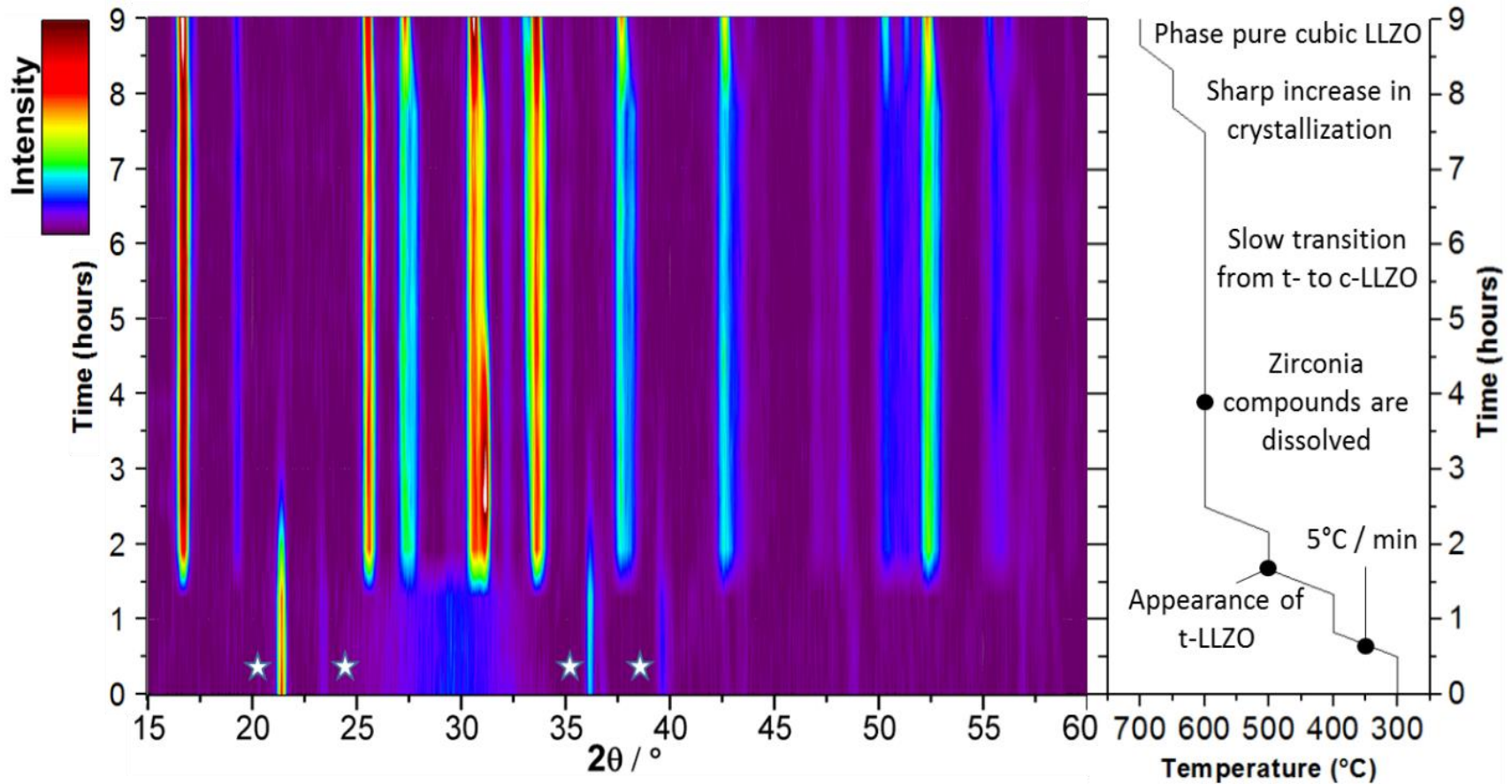
# Sputtering



# X-ray Diffraction

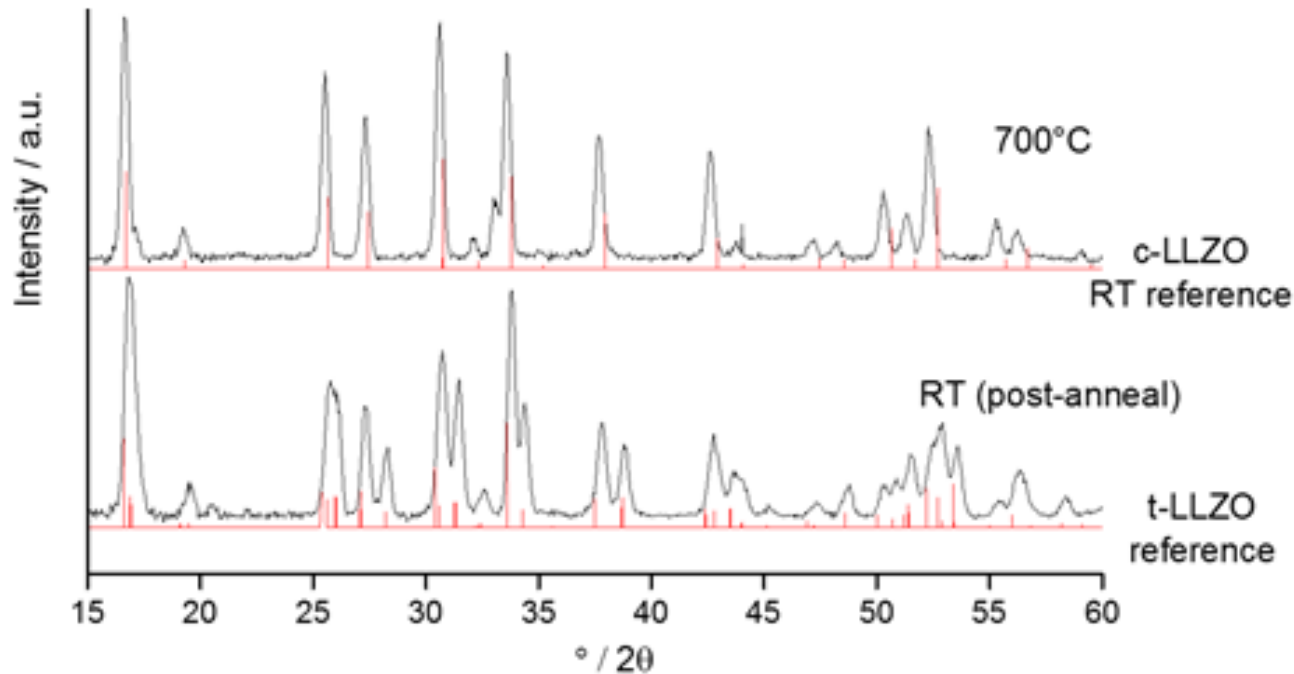


# In-situ XRD (LLZO no Ga)



Maram, Pardha S., Sergey V. Ushakov, Richard J.K. Weber, Chris J. Benmore, and Alexandra Navrotsky. *Journal of the American Ceramic Society* 98, no. 4 (2015): 1292–1299.

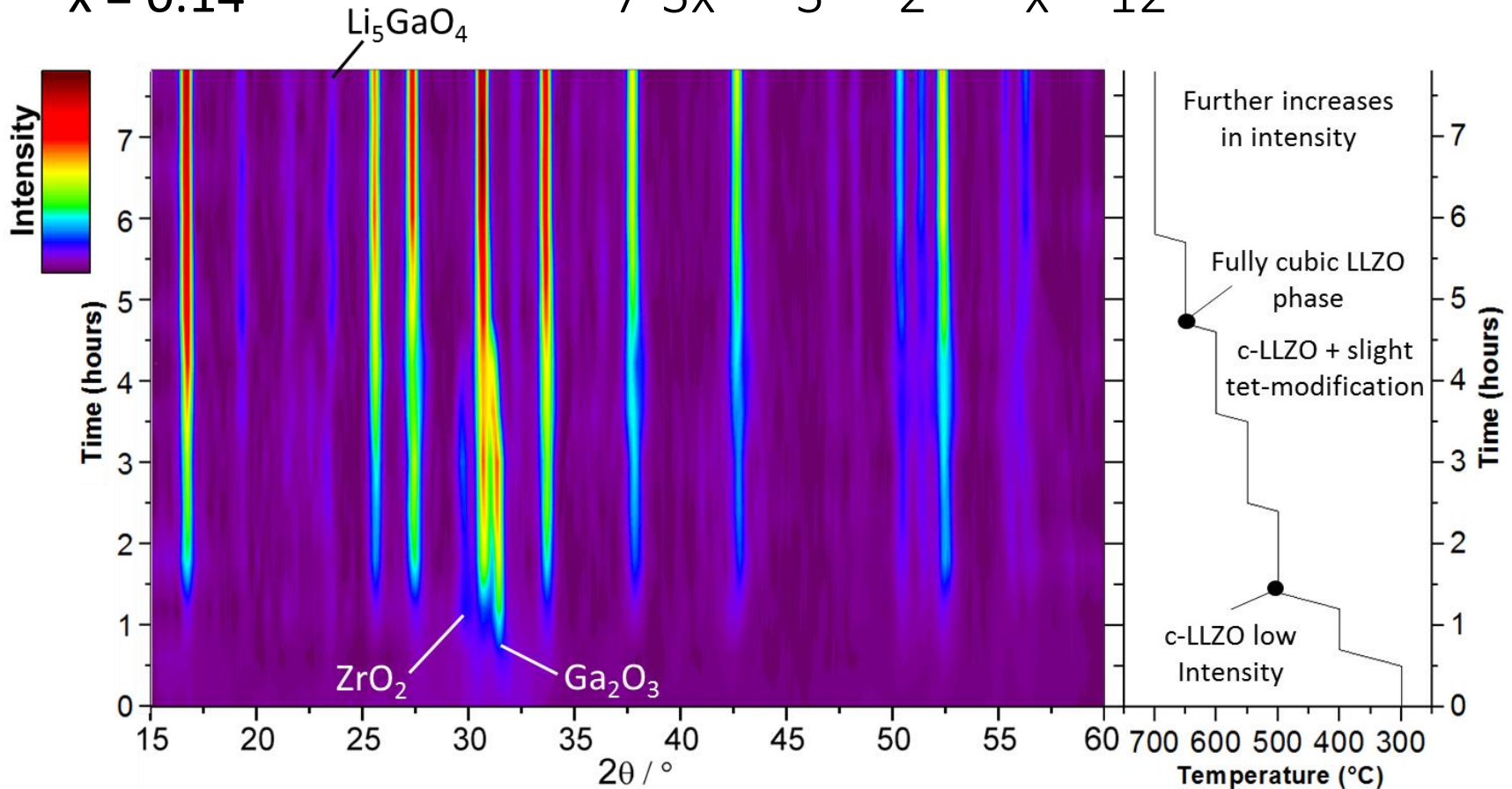
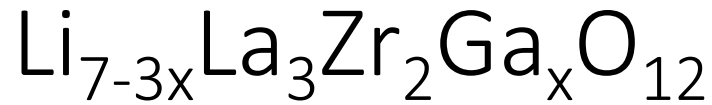
# In-situ XRD (LLZO no Ga)



- Formation of cubic phase c-LLZO at 700°C
- Conversion back to t-LLZO after cooling

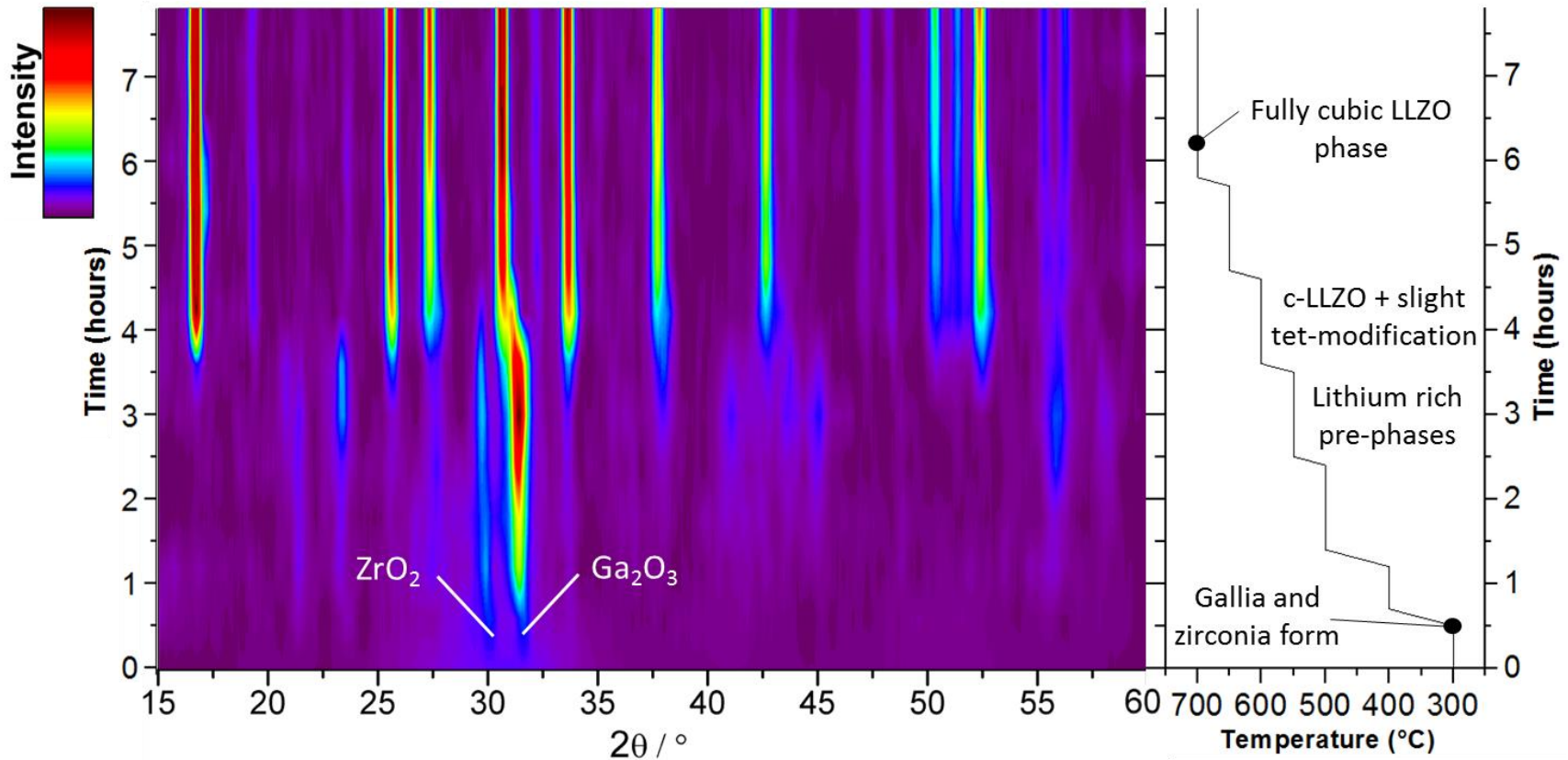
# In-situ XRD adding gallium

$x = 0.14$



# In-situ XRD adding gallium

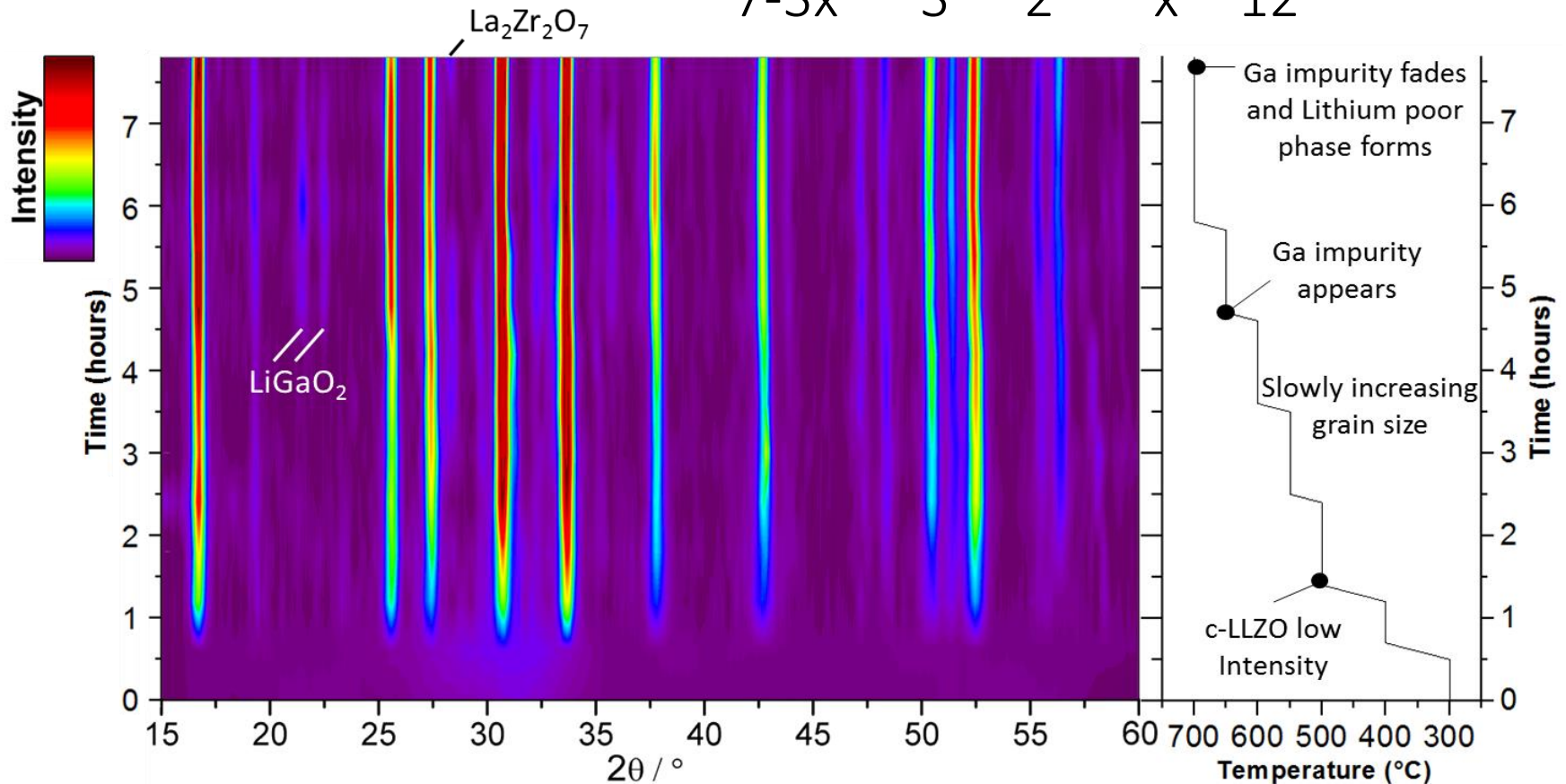
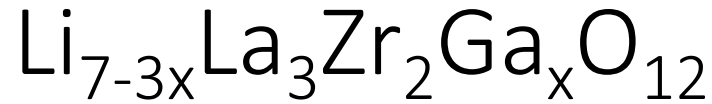
$x = 0.16$



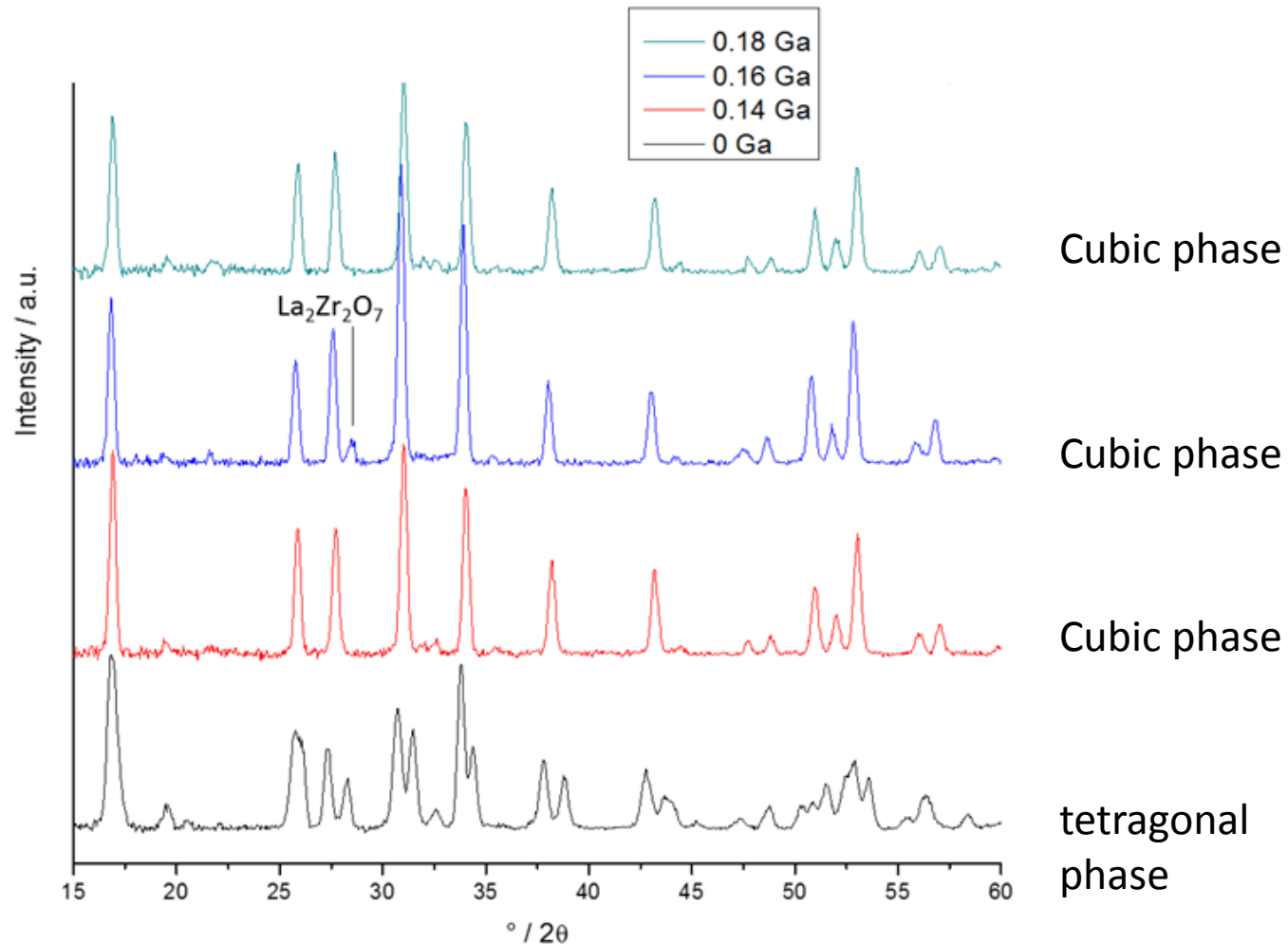


# In-situ XRD adding gallium

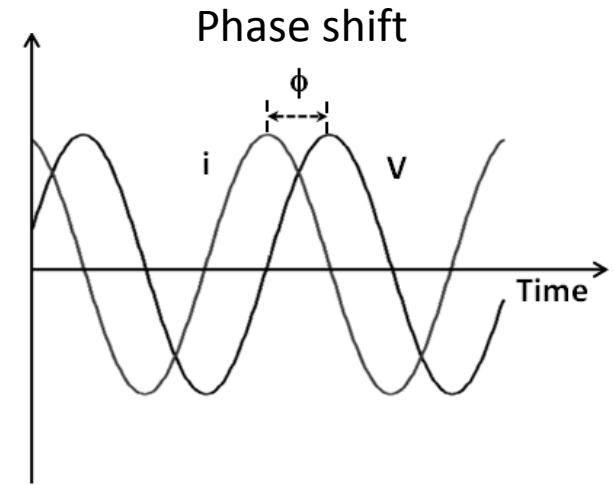
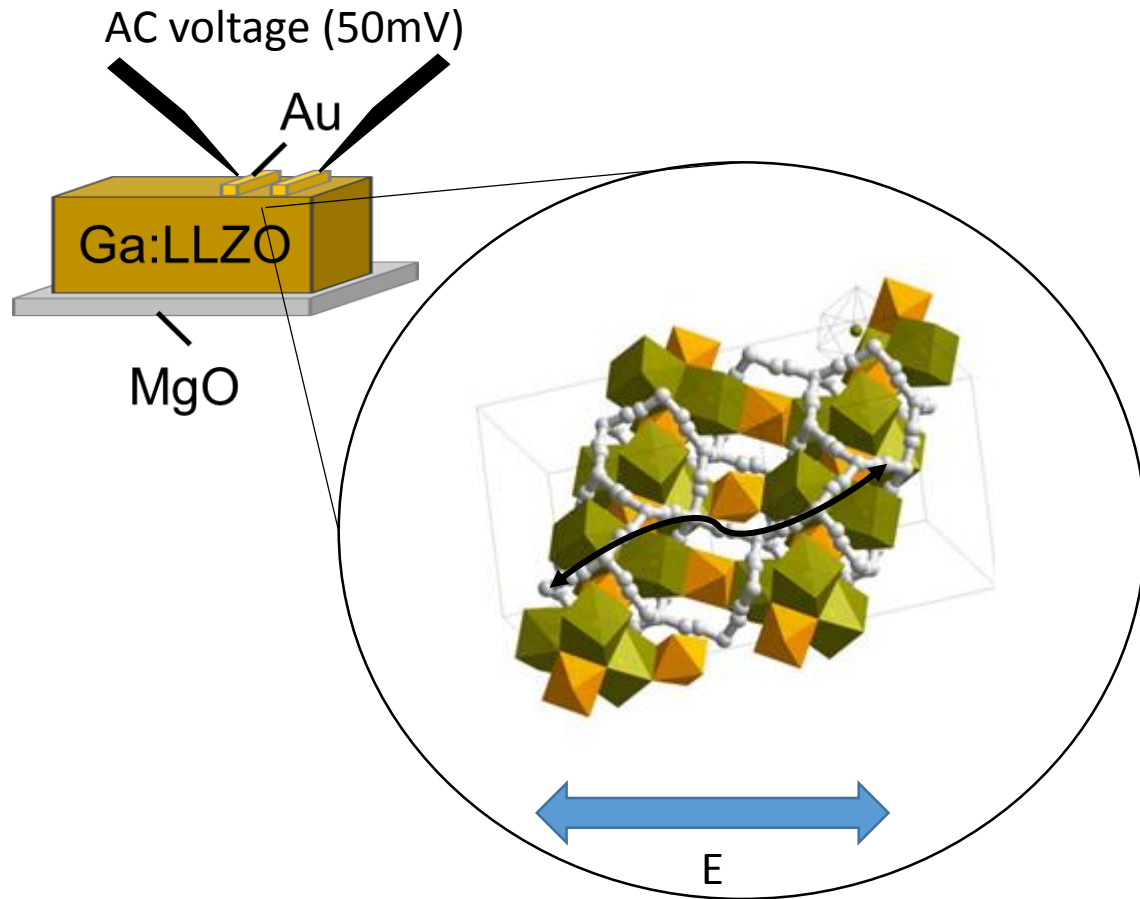
$x = 0.18$



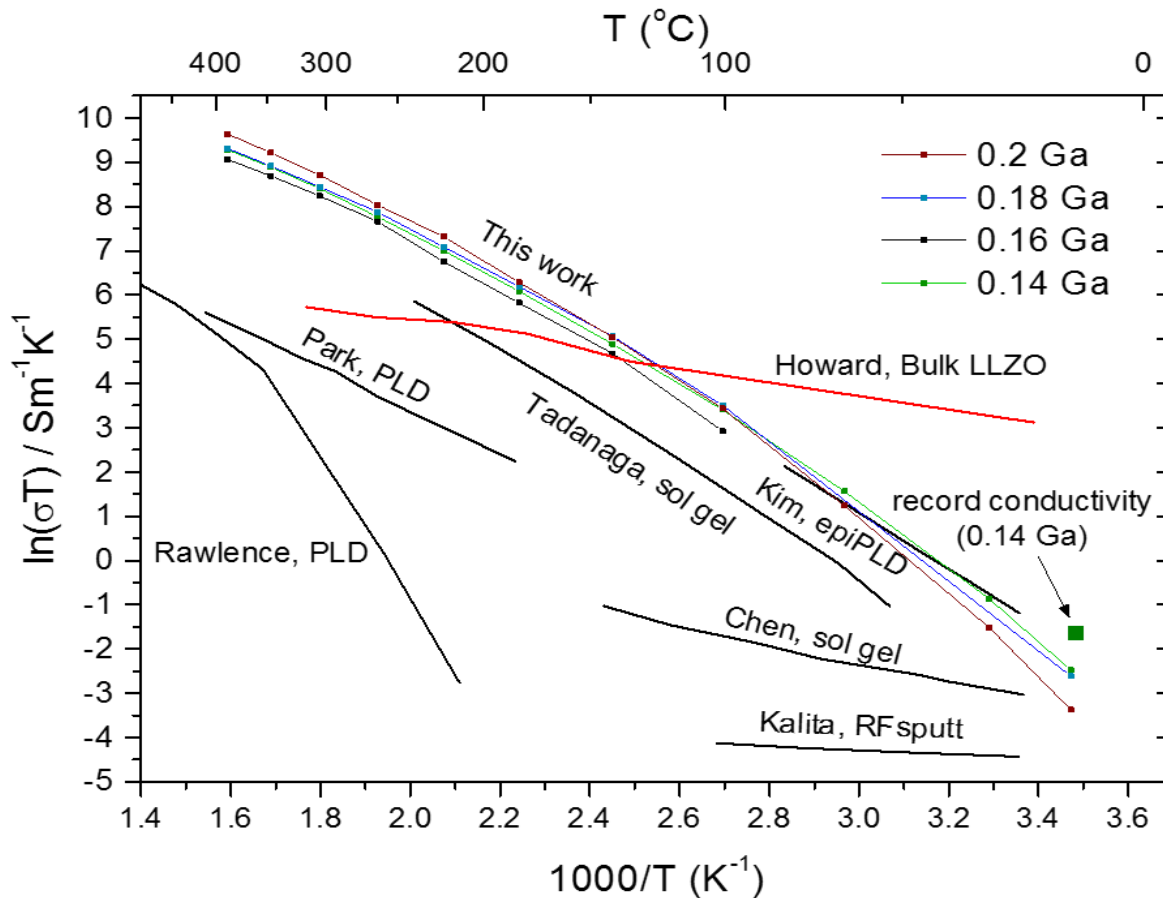
# Final XRD



# Impedance Spectroscopy



# Lithium ion Conductivity



$\sigma = 1.6 \times 10^{-5} \text{ S cm}^{-1}$  at RT!

❖ **Highest value** obtained so far for a Ga-doped **LLZO thin film**. Still improvement expected!

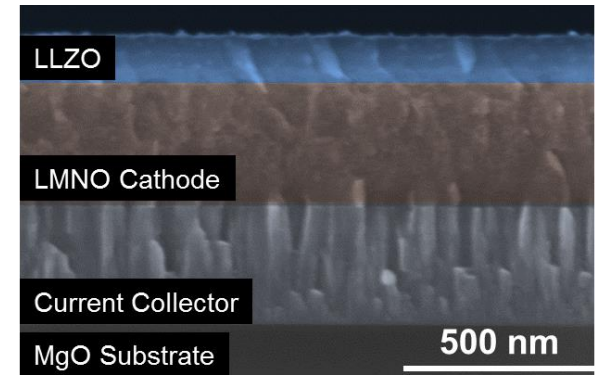
**Objective**  
 $\sigma \sim 1 \times 10^{-3} \text{ S cm}^{-1}$  (~ bulk)

# Conclusions

- Formation of the t-LLZO phase begins at 500°C and a conversion to c-LLZO begins above 650°C.
- Doping with gallium stabilizes the cubic phase at room temperature.
- Resulting conductivity of  $1.6 \times 10^{-5} \text{ S cm}^{-1}$  for 0.14 gallium per unit cell of LLZO. The highest value for thin film LLZO and x10 better than LiPON.
- Adding additional Ga is not advantageous for conductivity but can allow cubic LLZO to form earlier.

# Outlook

- Integrating the fast lithium ion conducting garnet into a full thin film battery.



- Lowering Processing temperature.

- Addition of interlayers to protect interfaces during processing.

# Thank you

Acknowledgements:

Competence Centre for Energy and Mobility – SLIB project  
*swisselectric*



ETH, Electrochemical Materials group

EMPA, Materials for Energy Conversion group