Phase Analysis of Conversion and Surface Reactions in LLZO Using Rapid Open-Air Plasma Synthesis

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Background

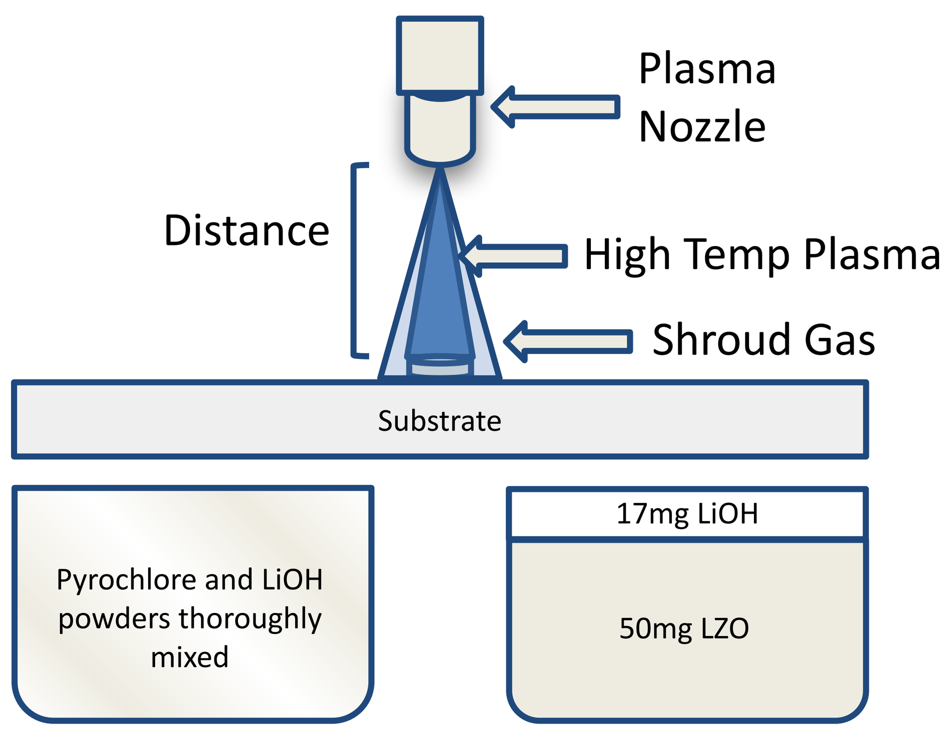
- Solid-state batteries offer improved safety and energy density compared to lithium-ion batteries
- **LLZO** ($Li_7La_3Zr_2O_{12}$) is a promising solid electrolyte due to high ionic conductivity and stability
- Conventional LLZO synthesis requires high temperatures and long furnace processing times
- LZO-LiOH systems enable a **pyrochlore-to-garnet** (LZO → LLZO) phase conversion
- Open-air plasma processing introduces surface reactions that can form impurities and incomplete conversion
- **P2G** (pyrochlore-to-garnet) processing is the conversion of LZO → LLZO through phase transformation pathways
- A key issue with P2G conversion is low density from LiOH decomposition, which creates pores and limits ionic conductivity measurements, which motivates the use of layered pellets to improve densification.

Goals

- Investigate plasma-driven conversion of LZO → LLZO
- Compare LZO-LiOH and P2G processing routes
- Identify any impurity phases and distinguish surface vs bulk effects
- Understand how plasma conditions affect LLZO formation

Method

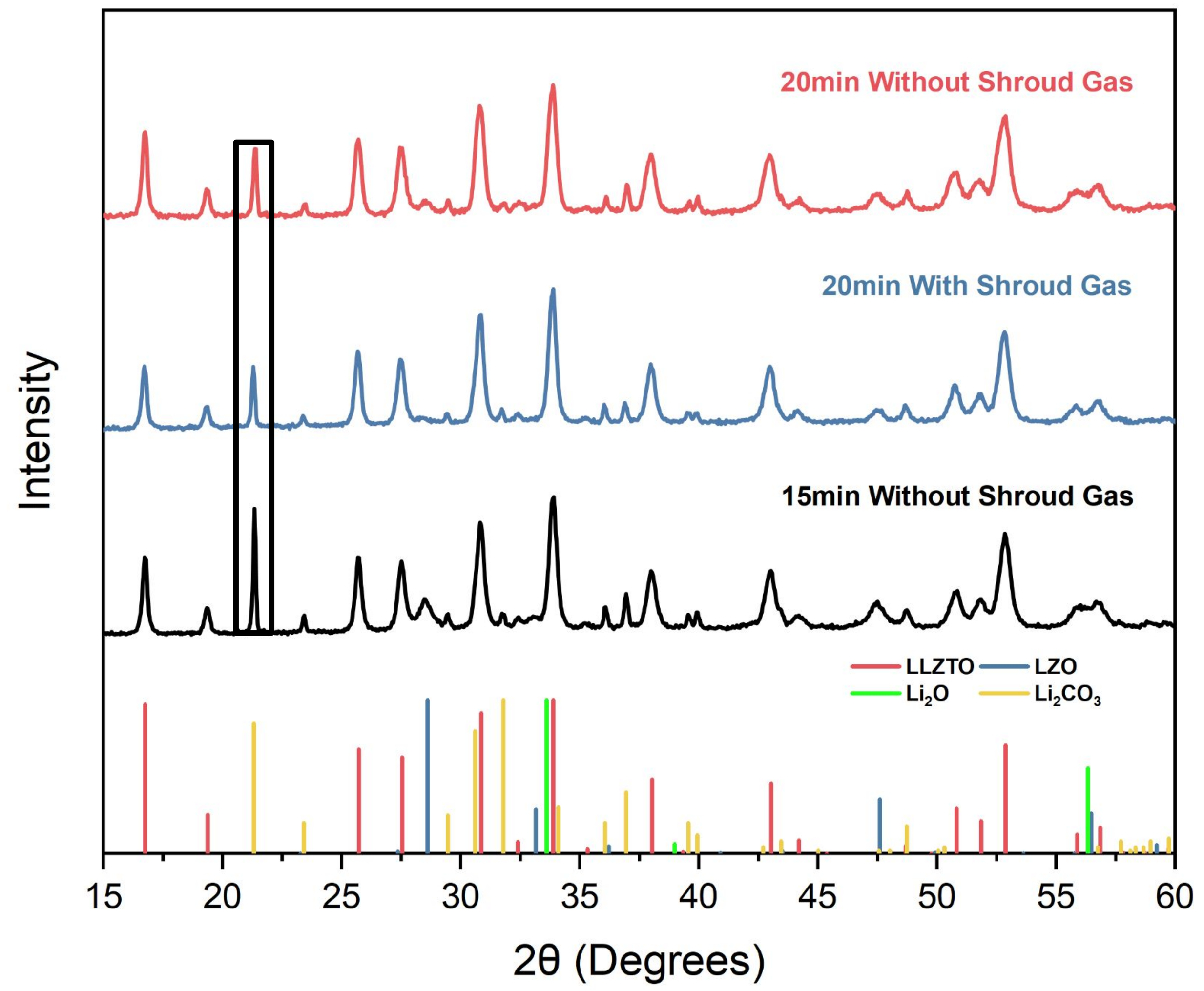
- Prepared layered LZO-LiOH pellets and P2G pellets
- Plasma-treated samples at 270–600°C (15–20 min)
- Varied distance, gas environment, and composition
- Shroud gas maintains a controlled cooling environment.
- Characterized phase evolution using XRD



P2G Mixed Pellets **Layered LZO-LiOH Pellets**

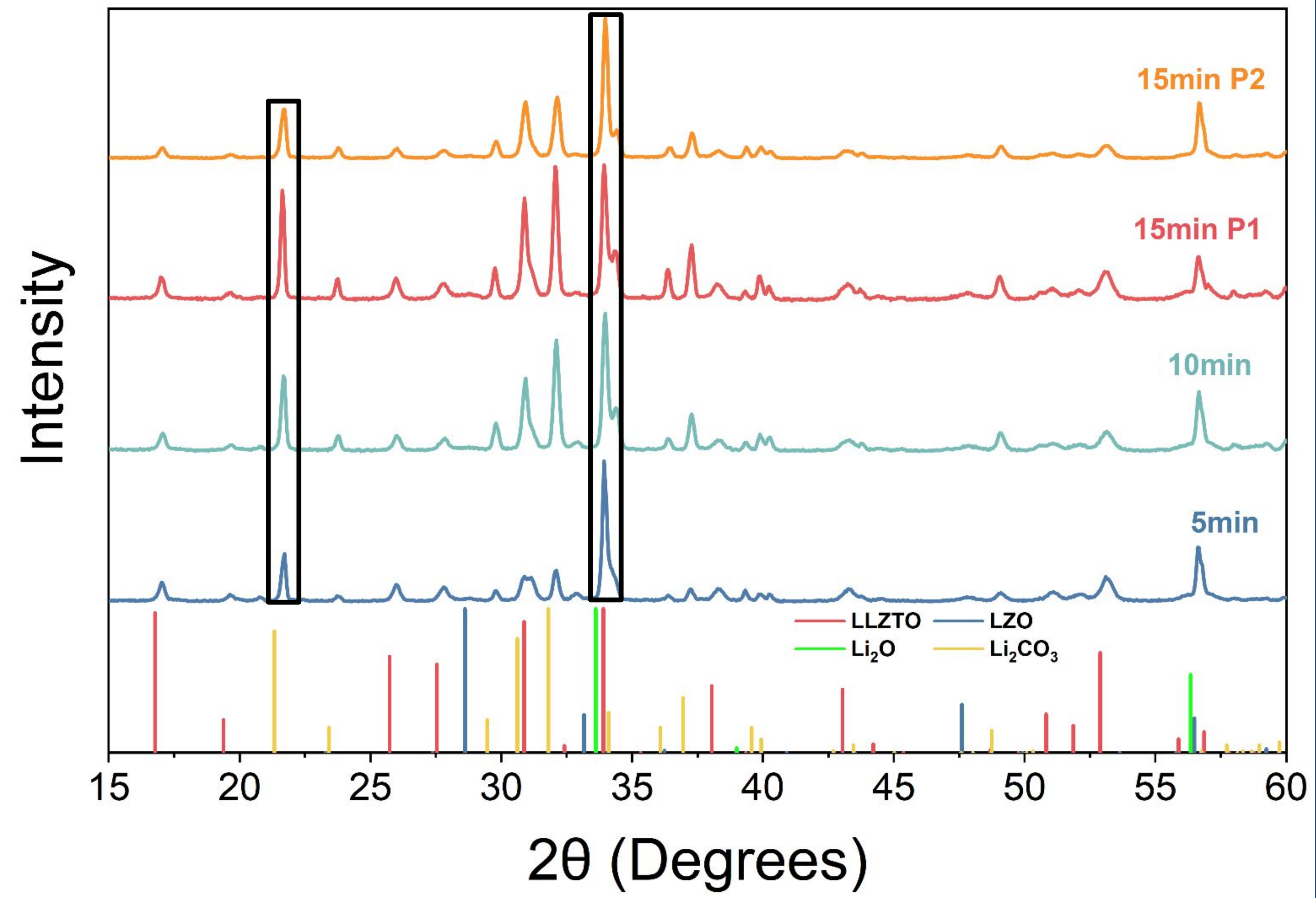
Results

P2G Mixed Pellet



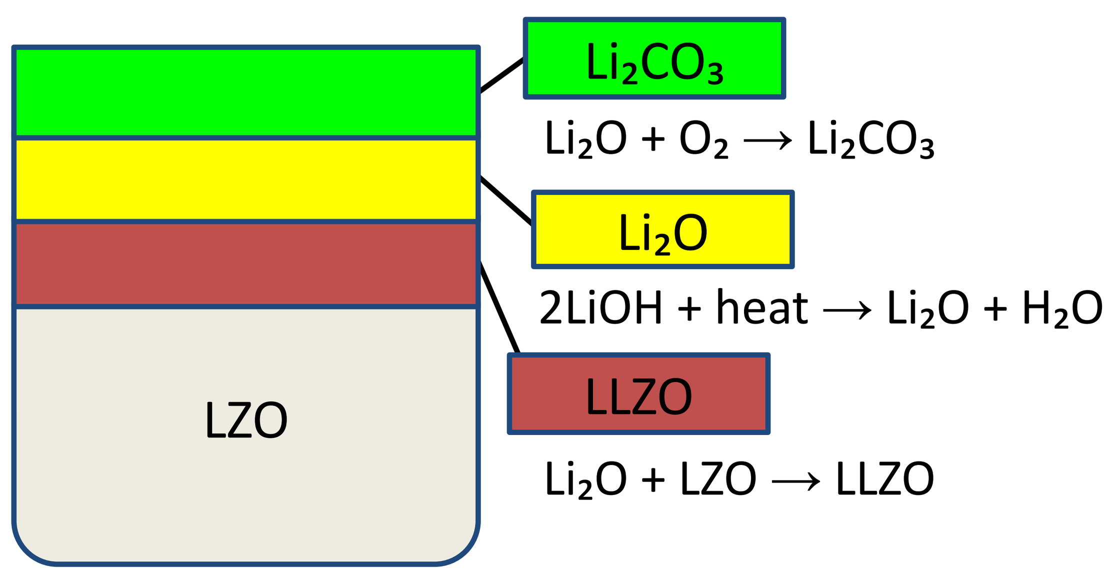
- All samples at 600°C
- Low density
- Better LLZO phase formation
- Impurity pathway differs
  - (peak only at ~21.7°)

LZO-LiOH Layered Pellet



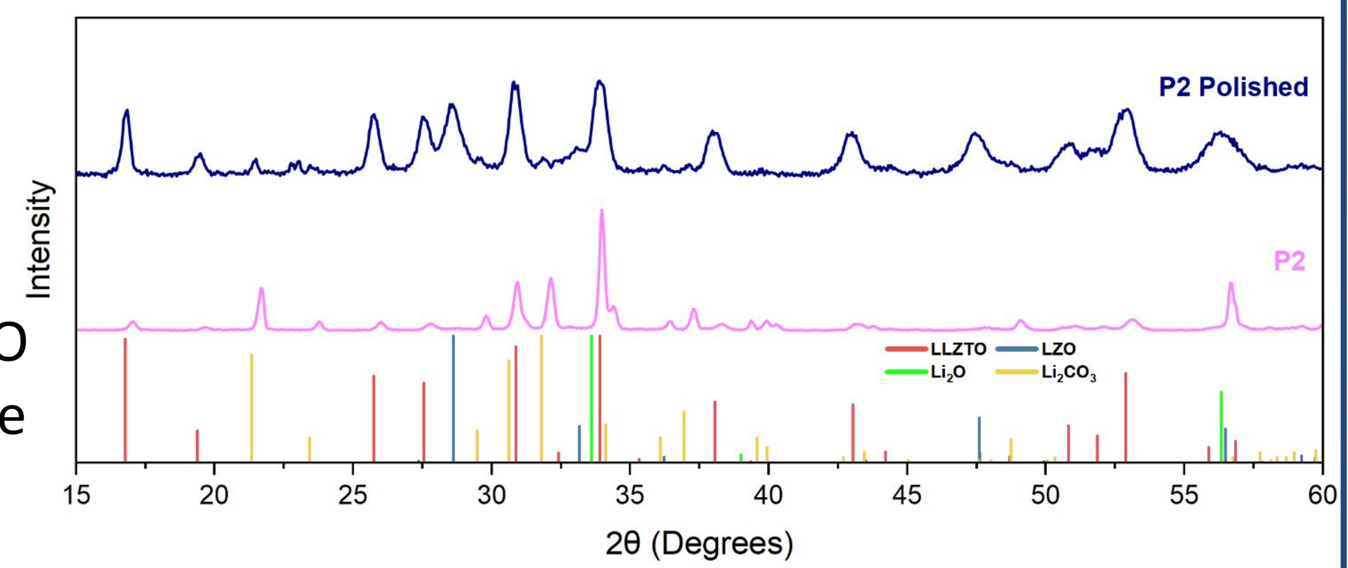
- All samples at 600°C with shroud gas
- Higher Density
- LiOH melts → flow issues → conversion issues
- Impurity at ~21.7° and ~34°
- P1 and P2 correspond to two similar 15 minute trials

LZO-LiOH Pellet Surface Reactions



Polishing:

- Lowers Li_2CO_3
- Reveals more LLZO
- Only some Li_2O remains



Conclusions

- Plasma processing enables LLZO formation at ~600°C, which is significantly lower than conventional sintering (>1000°C for hours)
- LZO-LiOH pellets show limited surface conversion due to LiOH melting and instability
- P2G processing improves LLZO formation but results in lower density
- Impurity formation is driven by surface reactions during plasma exposure
- Polishing reveals underlying LLZO beneath a surface impurity layer
- These results highlight a key tradeoff between phase formation and densification across processing routes

Outlook/Future

- Use a new plasma nozzle to achieve target temperatures at shorter distances and repeat prior experiments under improved conditions
- Further investigate and identify impurity phase occurring in P2G at 600°C
- Adjust plasma flow rate to control treatment distance while maintaining similar temperatures
- Better control LiOH melting in layered pellets to improve overall conversion

FURI

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