Deposition of Li-Garnet Thin Films for Characterization and Use in Solid-State Li-ion Batteries

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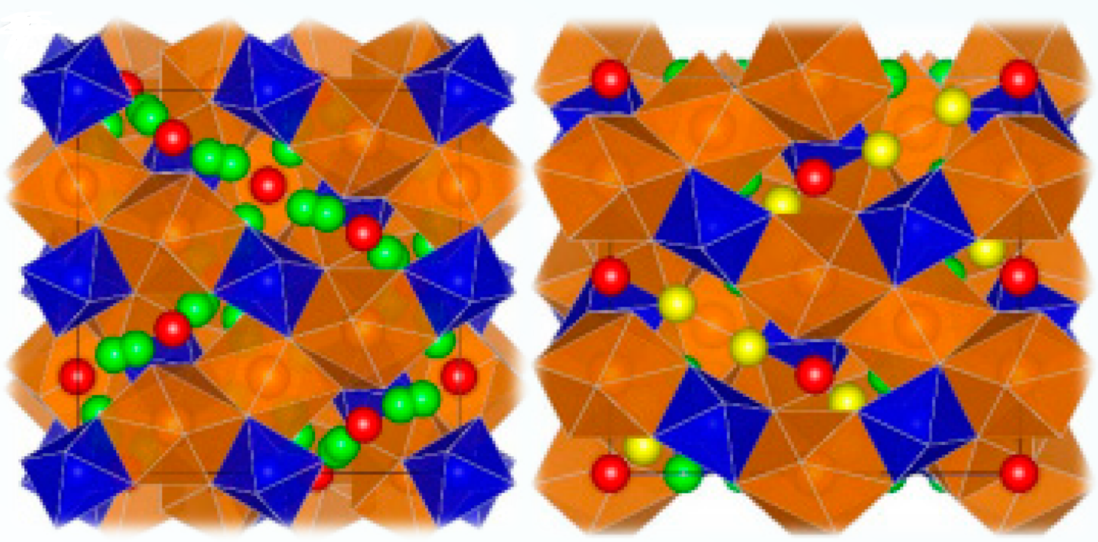
Introduction

Lithium-ion batteries are widely used for energy storage. Advantages the emerging technology of solid-state batteries over current liquid electrolyte batteries include:

- Greater product safety
- Higher energy densities

One of the most promising solid-electrolyte materials is LLZO ($Li_7La_3Zr_2O_{12}$), which forms two major crystalline structures:



c-LLZO (cubic) Ionic S: ~10^{-4} S/cm

t-LLZO (tetragonal) Ionic S: ~10^{-6} S/cm

[ZrO_6] Octahedron

[LaO_8] Dodecahedron

Only t-LLZO is thermodynamically stable at room temperature. However, the c-LLZO phase can be stabilized by the addition of metal dopants. This study investigates the deposition of Ta-doped LLZO.

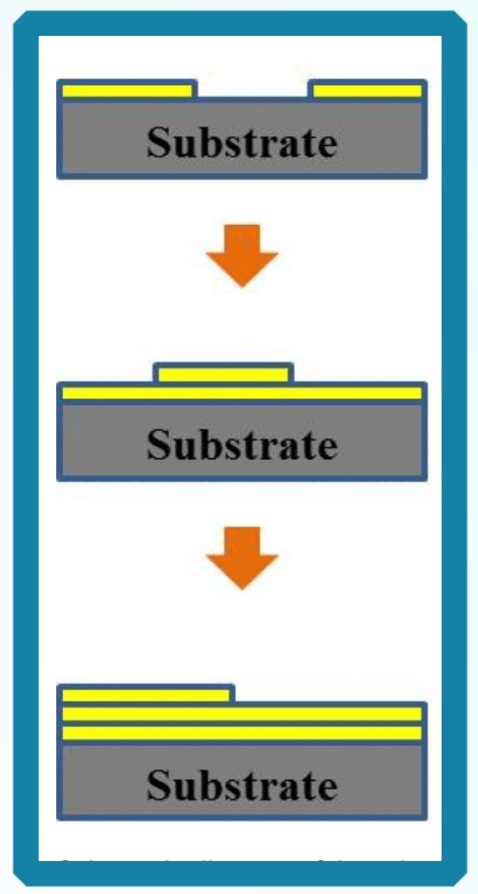
Thin film LLZO electrolytes may allow for greater power density than bulk pellets, as they reduce volume, weight, and area-specific electrolyte resistance. Current challenges to thin-film LLZO causing lower ionic conductivity include:

- Impurities in the deposition
- Lithium depletion

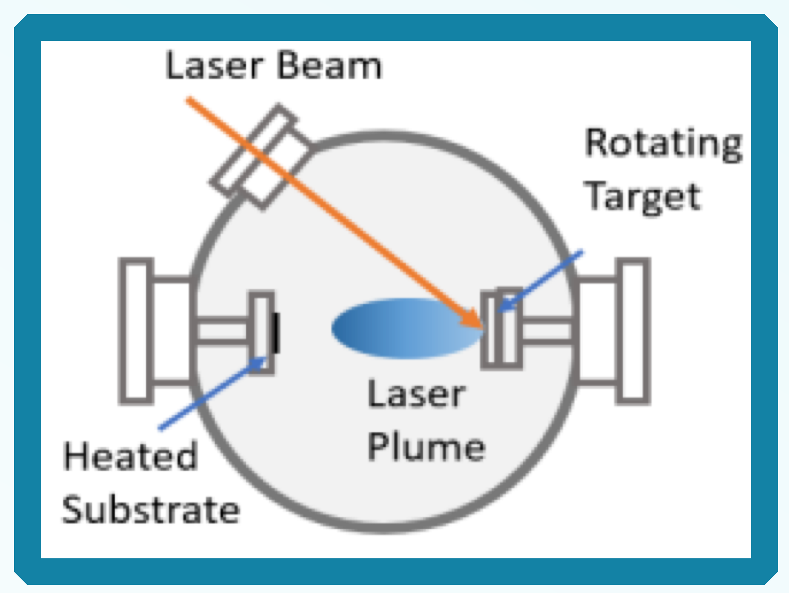
Methods – Pulse-Laser Deposition

Lithium depletion issues are addressed by layering LLZO with Li_2O during the deposition.

MgO substrate was used to promote epitaxial growth, in order to reduce impurities, grain boundaries, and other barriers to conductivity.



Schematic of layer-by-layer epitaxial growth

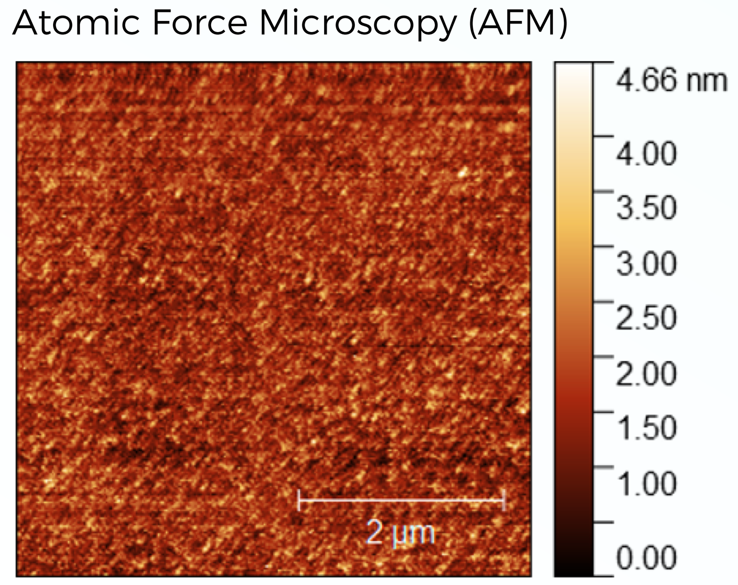


Schematic vacuum PLD chamber

Parameters that were varied between depositions:

- Temperature
- O_2 deposition pressure
  - Increasing pressure resulted in a visibly denser plume
- LLZO/ Li_2O pulse ratio
- Rate of deposition (laser pulses per second)
- Number of layers

Atomic Force Microscopy (AFM)



AFM was used to determine sample roughness.

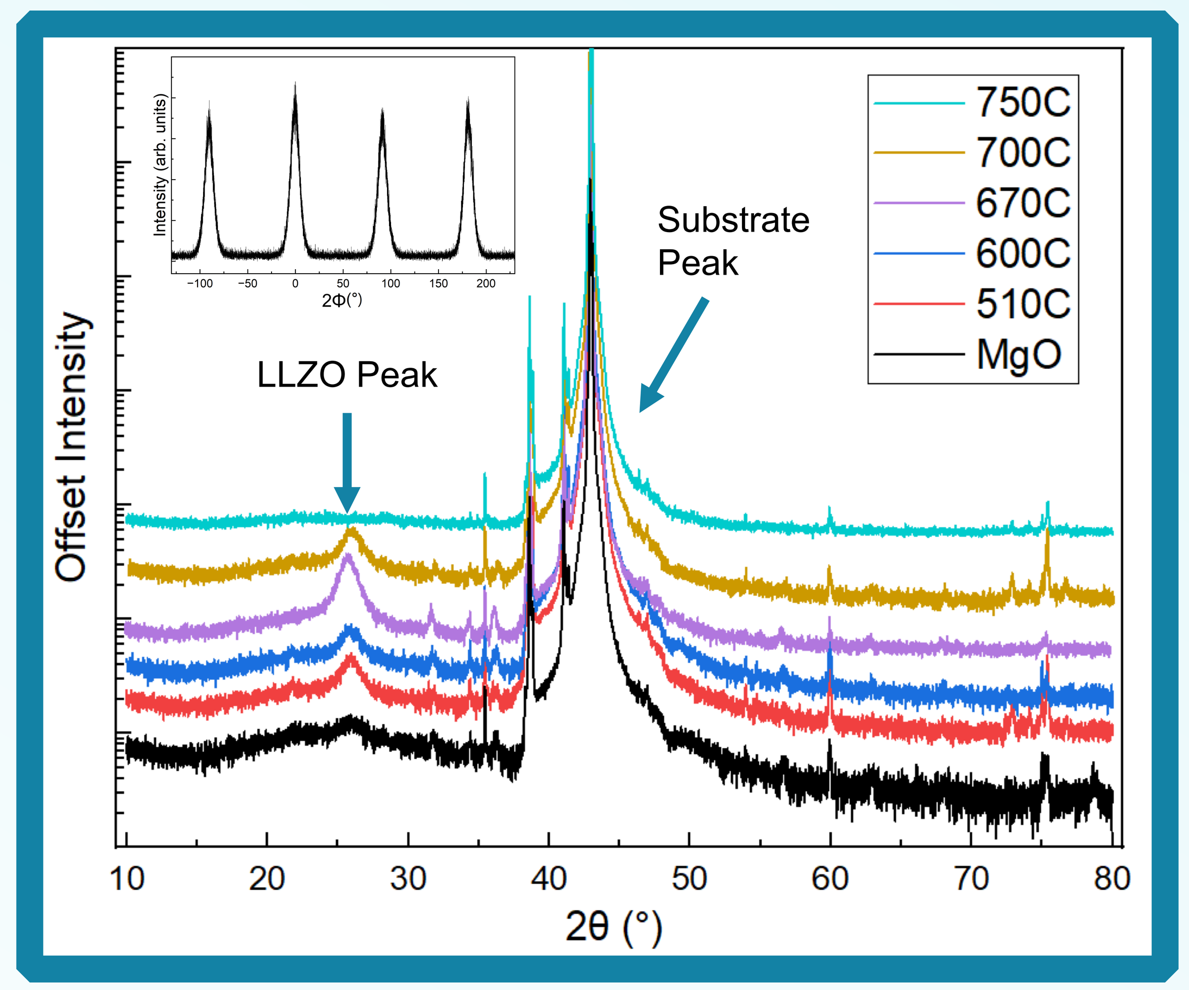
Average rms of samples: 0.5 nm

Increasing rate of deposition and sample exposure to air caused increased surface roughness.

Results

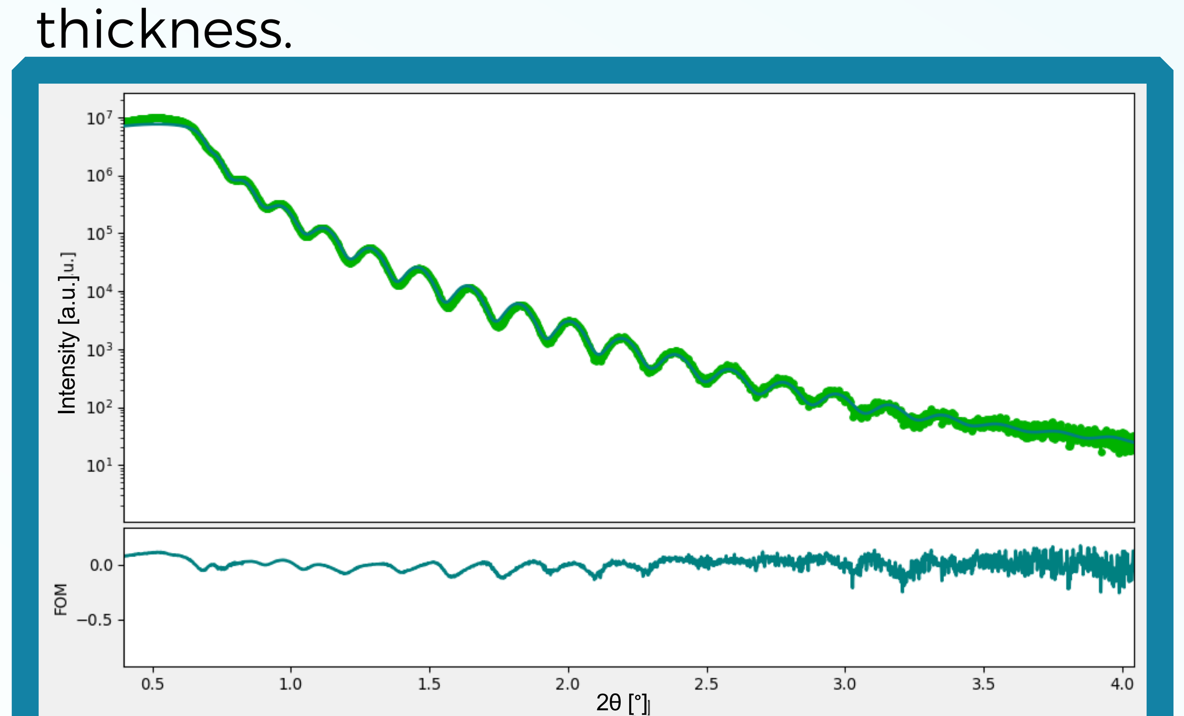
X-ray diffraction data was used to characterize deposited films. Initial results suggest 4-fold symmetry.

Samples deposited at extreme temperatures were less likely to show the LLZO peak.



XRD Data, with visible substrate and LLZO peaks at various deposition temperatures. Inset: XRD phi scan

X-ray reflectometry (XRR) was used to measure an average of 50 nm in film thickness.



Conclusions and Future Work

Further testing is required to confirm the phase of LLZO deposited, and whether the epitaxial deposition was successful.

Films had good roughness and thickness.

Deposition conditions (laser voltage, O_2 pressure, etc.) may need to be changed to ensure adequate Li_2O concentration.

Samples are being produced and sent to NIST for further characterization experiments:

- Effectiveness of LiPF soaking at removing contaminants (Li_2CO_3)
- Preliminary results on effectiveness of a mixed-phase electrolyte using LLZO film and LiPF solution – allowing usage of lithium metal anodes
- XPS and neutron reflectometry

Later studies will need to determine the ionic conductivity of the Ta-LLZO / Li_2O multilayer films, as well as rates of interfacial resistance between film and electrode.

Acknowledgments

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