Contract No:

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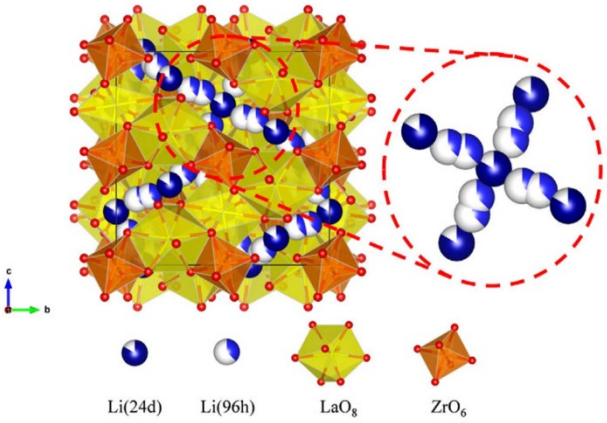
LDRD-2020-00079
LDRD External Report Summary

Title of Project
Solid State Ionics: Materials Development by Multiscale Modeling and Advanced Manufacturing Techniques

Project Start and End Dates
Project Start Date: 10/1/2019
Project End Date: 9/30/2021

Project Highlight
This project advances our fundamental understanding of solid-state ionic materials and enables new highly efficient processing techniques for energy conversion and storage device applications. Specifically, this research addresses compositional development through density functional theory and molecular dynamic simulations, explores the impact of microstructural modifications on optimized compositions, and demonstrates advanced manufacturing consisting of 3D laser processing for the deposition of thin film ion conductors in the form needed for a wide range of ceramic energy conversion and storage devices of interest to the Department of Energy.



Project Team
Principal Investigator: Lindsay Roy
Team Members: Dale Hitchcock, Christopher Dandeneau, Brenda Garcia-Diaz, Chandler Hawsey, Patrick Kuzbary
External Collaborators (all external collaborators and their respective organizations that participated in this project: Kyle Brinkman, Lindsay Shuller-Nickles, Clemson University

Abstract
Solid-state ionic materials are an important enabling technology for energy conversion and storage. Solid-state batteries would be a safer and higher energy density alternative to commercially available lithium ion batteries (LIB), however their implementation requires ion conduction in solids at room temperature to occur on the same level as the current generation of liquid electrolytes. Microstructural modifications have been demonstrated to play a major role on ion transport through the control of grain boundary interfaces, which traditionally serve as “blocking” layers. Ultimately, these materials will be fabricated in thin films form as electrolytes in order to minimize ohmic losses in electrochemical devices. This work uses advanced manufacturing techniques in combination with theoretical modeling to implement a science-based approach in the deposition of thin films ion conductors with controlled microstructures used in ceramic energy conversion and storage devices.

FY21 Objectives
- Microwave solution combustion synthesis (SCS) of pure cubic phase LLZO
- Electrochemical characterization of bulk and laser sintered LLZO
- Bulk defect incorporation and Li+ ion mobility calculations
- Defect migration and grain boundary energetics

- Solid state laser sintering of Ga-doped and Ta-doped LLZO
- Energy conversion device manufacturing

Reviews and Approvals

1. Authors:

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Name and Signature Date

2. Technical Review:

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Name and Signature Date

3. PI's Manager Signature:

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Name and Signature Date

4. Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

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Name and Signature

LDRD-2020-00079
LDRD External Report Summary

Introduction

Solid-state ionic materials are an important enabling technology for energy conversion and storage. While solid-state batteries would be a safer and higher energy density alternative to commercially available lithium ion batteries (LIBs), their implementation requires ion conduction in solids at room temperature to occur on the same level as the current generation of liquid electrolytes. Microstructural modifications have been demonstrated to play a major role in ion transport through the control of grain boundary interfaces, which traditionally serve as "blocking" layers. Ultimately, these materials will be fabricated in thin film form as electrolytes in order to minimize ohmic losses in electrochemical devices. This work uses advanced manufacturing techniques (e.g., 3D printing followed by laser processing) in combination with theoretical modeling to implement a science-based approach in the deposition of thin film ion conductors with controlled microstructures that are employed in ceramic energy conversion and storage devices.

Specific focus has been placed on the use of aliovalent dopants in Li-ion conducting $Li_7La_3Zr_2O_{12}$ (LLZO) with a garnet-like structure.[1] Although the thermodynamically stable tetragonal phase of LLZO exhibits relatively low Li^+ conductivity, dopants such as Ga^{3+} on Li sites or Ta^{5+} on Zr sites stabilize the cubic polymorph of LLZO thereby producing increases in both the Li vacancy concentration (for charge compensation) and ionic conductivity by two orders of magnitude.[2,3] However, the preparation of doped LLZO remains challenging because conductivity is dependent upon control of the dopant concentration *i* and conditions necessary to suppress the sublimation of volatile Li during sintering are dependent upon variables that are difficult to quantify or control. To overcome these challenges, research has focused on tailoring the appropriate microstructure with fast manufacturing techniques and computational evaluations to enable significant progress toward understanding and controlling the microstructure of LLZO. Specifically, our results have shown that advanced quantum calculations can predict the precise dopant concentration necessary for rapid Li^+ migration, while fabrication techniques such as solid-state reactive sintering (SSRS) enable enhanced materials processing at lower temperatures.

Overall, this project addresses key scientific issues identified by the Department of Energy (DOE) – Basic Energy Science (BES), Fusion Energy Science (FES) and Energy Efficiency and Renewable Energy (EERE) program that limit the present understanding and implementation of solid-state ionic materials and devices in separations, energy conversion and storage applications. Key issues include the utilization of experimental and computational methods to elucidate phenomena related to ionic transport through the bulk of materials and across interfaces (e.g. grain boundaries, surfaces, and layers of functional devices). Since polycrystalline materials are likely to find widespread usage as low-cost and scalable energy conversion devices, an understanding and ability to tailor the microstructure of such compounds via fast manufacturing routes is essential to the development and implementation of new materials.

Approach

This project incorporates a three-pronged approach as summarized in Figure 1. Task A focuses on novel synthetic and characterization methods such as solid-state reaction synthesis (SSRS) and solution combustion synthesis (SCS) for rapid and efficient materials production. Task B utilizes quantum mechanical calculations to help inform the experimental thrust by correlating the thermodynamic stability of doped LLZO with observables such as X-ray diffraction (XRD) and X-ray absorption spectroscopy data. Task C sets out to fabricate dense 3D thin films of doped LLZO followed by rapid laser sintering. Each box represents a subtask in the project and the items highlighted in green were completed during this project. Those in light green are in progress and will be pursued for follow-on funding.

Accomplishments

The project work was divided into three tasks: Progress in all areas along with the FY21 milestones for each task are outlined below. Results and accomplishments are presented under each milestone.

- Task A: Materials Synthesis and Characterization
  - M5: Microwave solution combustion synthesis (SCS) of pure cubic phase LLZO (Dec 2020)
    - The feasibility of fabricating single-phase cubic LLZO via microwave-assisted solution combustion synthesis (SCS) is investigated. SCS involves the initiation of a thermodynamically favorable, self-sustaining redox reaction between metal nitrates (oxidizers) and suitable fuels. The intermixing of molecular components in solution allows for excellent compositional control, while the simplicity of the process facilitates ease of scalability and the use of modular components.
    - Undoped, Ga-doped, and Ta-doped LLZO compositions were prepared via SCS.
    - Initial studies demonstrated the formation of undoped, single-phase tetragonal LLZO using $LiNO_3$, $ZrO(NO_3)_2$, and $La(NO_3)$ precursors with urea as a fuel (Figure 2). Subsequent X-ray photoelectron spectroscopy (XPS) analysis showed Zr occupying only one site in the LLZO lattice, thereby indicating an absence of trace secondary $La_2Zr_2O_7$ phases in the material (Figure 3).
    - Ga-doped LLZO with composition of $Li_{5.5}Ga_{0.5}La_3Zr_2O_{12}$ was fabricated via SCS using $Ga(NO_3)_3$ as precursor. Calcination at 950 °C for 5 h yielded single-phase LLZO with a cubic garnet structure (Figure 4).
    - Single-phase Ta-doped LLZO with composition of $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ was also fabricated via SCS and characterized by XRD. The preparation of Ta-doped LLZO is complicated by the lack of a Ta nitrate precursor. Here, Ta-oxalate solutions were prepared and NH_4NO_3 added to compensate for lack of an oxidizing component. Additionally, H_2O_2(30%) was utilized as a catalyst to break up hydrated tantalum oxide and facilitate dissolution/complex formation with oxalic acid.
    - Peer-reviewed manuscript in preparation to be submitted in November 2021. It will focus on the synthesis of single-phase undoped and Ga-doped LLZO via SCS.
  - M6: Electrochemical characterization of bulk and laser sintered LLZO (May 2021)
    - Ionic conductivity of SCS-derived Ga-doped LLZO was measured from room temperature to 370 K. The obtained ionic conductivity was low (1.8×10^{-6} S/cm), likely due to the low density of the sintered material. Future work is aimed at optimizing the sintering protocols for the SCS-derived powder.
- Task B: Multiscale Modeling
  - M4: Bulk defect incorporation and Li+ ion mobility calculations (Mar 2020)
    - In Ga-doped LLZO systems, the most stable configuration is when the interatomic distances between Ga dopants (*i.e.*, $Ga_{Li}^{\cdot\cdot} - Ga_{Li}^{\cdot\cdot}$ distances) and between Ga dopants and Li vacancies (*i.e.*, $V_{Li}^{\prime} - Ga_{Li}^{\cdot\cdot}$ distances) are minimized. Thus, defect clustering contributes to an energetic stabilization of the overall system until the solubility limit is reached. The U-shaped reaction energy (Figure 5) with respect to concentration emphasizes the complexity of the thermodynamic interplay that

exists between endothermic (e.g., Li-loss, vacancy formation) and exothermic (e.g., vacancy ordering and aggregation) processes. In general, the formation of Li defects and Li defects clustering is an endothermic process considering the effect of increased organization in the system, particularly for clustering of same charged defects.

- Submitted peer-reviewed manuscript in December 2020. Paper identified Coulomb energy and DFT calculations were used to evaluate Li-site configuration. Energetic evaluation of Ga-doped LLZO ($Li_{7-3x}Ga_xLa_3Zr_2O_{12}$ where x=0, 0.125, 0.25, 0.5, 0.75, 1.0) was performed. Theoretical thermodynamic stability was used to investigate local coordination environments of Ga. Ga-concentrations, as well as crystal lattice parameters, were correlated with theoretical thermodynamic stability (under revision).
- MRS conference presentation: "Computational Insights of Ga-Doped LLZO with DFT Investigations".
- ACS conference invited presentation: "Solid State Ionics: Materials Development by Multiscale Modeling and Advanced Manufacturing Techniques".

– M7: Defect migration and grain boundary energetics (Aug 2021 Go/No Go)

- Preliminary calculations to understand Li-ion transport at the grain boundary examined two low-energy grain boundaries of Ta-doped LLZO (Figure 6). Molecular dynamics simulations found that Li transport is dependent upon structure and temperature. Transport in $\Sigma 3$ remains relatively fast (near the bulk rate) while transport at the $\Sigma 5$ boundary is roughly 3 order of magnitude slower.
- Peer-reviewed manuscript in preparation to be submitted December 2021. Paper will also outline FY20 calculations on the computed energies and structural changes within the Ta-doped LLZO ranging from 25% to 75%. Systems doped around 50% Ta retain the symmetry needed for facile Li+ mobility; higher doped systems are lower in energy but break the necessary symmetry needed for Li+ mobility.

- Task C: Advanced Manufacturing

– M8: Solid state laser sintering of Ga-doped and Ta-doped LLZO (Feb 2021 Go/No Go)

- Two models were developed to predict the average crystallite size as a function of sintering temperature and time using different algorithms including Random Forest regression and fitting to a known grain growth kinetic equation. Due to the limited number of data points, all data were utilized in the training of each model. Figure 7 shows a plot of average crystallite size vs sintering time where the dots correspond to experimental data points and the lines correspond to the Random Forest regression model fit. The average training error for this model was 1.54% with an R squared value of 0.955. Figure 8 shows a plot of average crystallite size vs sintering time where the dots correspond to experimental data points and the lines correspond to the grain growth model fit. The average training error for this model was 9.25%, however, the figure shows that the model was unable to accurately describe the variability in the data. This can be seen from the fact that the model prediction lines are near straight whereas the data points show a logarithmic behavior.

- The error analyses show that the Random Forest regression algorithm provides the best ability to model the sintering process for Ta-doped LLZO. This shows that the sintering process can be modeled using machine learning methods and future work in this area can expand upon these results.

– M9: Energy conversion device manufacturing (Aug 2021)

- Work has started on the additive manufacturing based micro extrusion, modified micro extrusion by doctor blade smoothing, spray coating, and inkjet printing to allow the manufacturing of LLZO thin layers with thickness from 5-2000 µm. Combined with laser cutting, more precise complex shapes can also be fabricated. The laser processing can make the fully dense membrane, highly porous membrane from cost-effective raw materials of carbonates and oxides, etc. The proper sintering additives are the critical factor for achieving crack-free large-area parts by rapid laser reactive sintering.

Future Directions

Further work in this area includes optimization of the sintering protocols for the SCS-derived powder, expansion of the modeling of grain boundary energetics, use of ML methods to predict the average crystallite size as a function of sintering temperature and time, and research into additive manufacturing of LLZO thin films. Funding has started in fusion related activities through ARPA-E, and we are planning to communicate these findings to DOE-EERE AMO for follow-on funding in energy conversion and storage devices.

References

1. Han, F.; Zhu, Y.; He, X.; Mo, Y.; Wang, C., Electrochemical Stability of Li10GeP2S12 and Li7La3Zr2O12 Solid Electrolytes. *Advanced Energy Materials* **2016,** *6* (8), 1501590.
2. Wagner, R.; Redhammer, G. J.; Rettenwander, D.; Senyshyn, A.; Schmidt, W.; Wilkening, M.; Amthauer, G., Crystal Structure of Garnet-Related Li-Ion Conductor Li7–3xGaxLa3Zr2O12: Fast Li-Ion Conduction Caused by a Different Cubic Modification? *Chemistry of Materials* **2016,** *28* (6), 1861-1871.
3. Gu, W.; Ezbiri, M.; Prasada Rao, R.; Avdeev, M.; Adams, S., Effects of penta- and trivalent dopants on structure and conductivity of Li7La3Zr2O12. *Solid State Ionics* **2015,** *274*, 100-105.

FY 2021 Peer-reviewed/Non-peer reviewed Publications

"Thermodynamic stability and Li+/vacancy distribution of Ga-doped LLZO: Insight into dopant-enhanced Li+ mobility," Changlong Li, Lindsay Roy, and Lindsay Shuller-Nickles, manuscript in review, Clemson lead institution.
"Energy Storage Through Materials Science," SRNL Matter Publication

Intellectual Property

None

Total Number of Post-Doctoral Researchers

Akihiro Ishii, Clemson University, Advisor: K. Brinkman
Eric Hoar, Savannah River National Laboratory, Advisor: L. Roy

Total Number of Student Researchers

Changlong Li and Rahul Rajeev, Clemson University, Advisors: K. Brinkman and L. Shuller-Nickles

Include all images, charts, and figures with captions, as shown below.

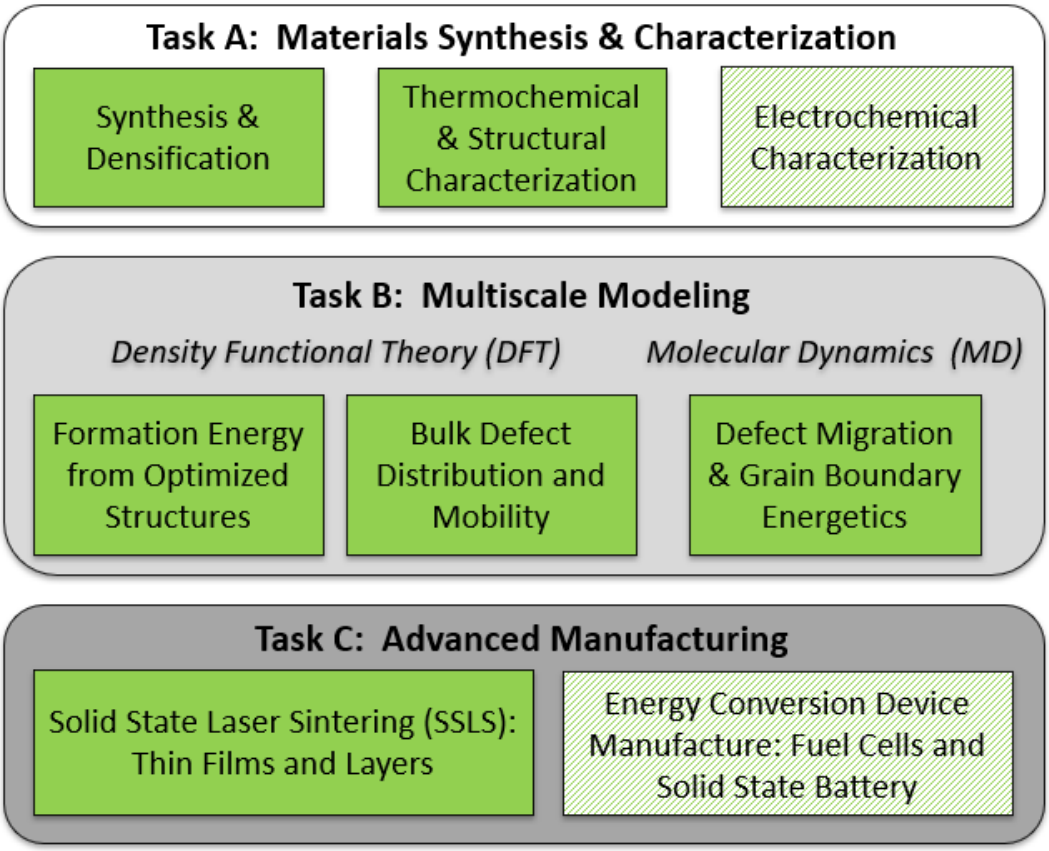

Figure 1. Pictorial representation of the approach used in this project.

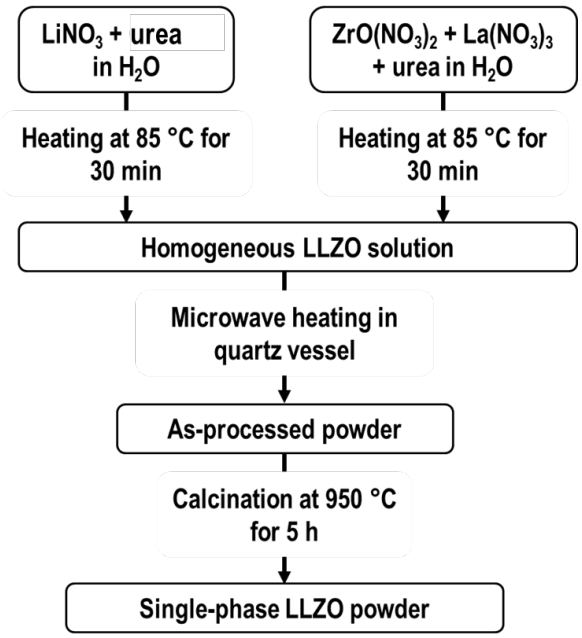

Figure 2. Diagram of the SCS process for undoped LLZO.

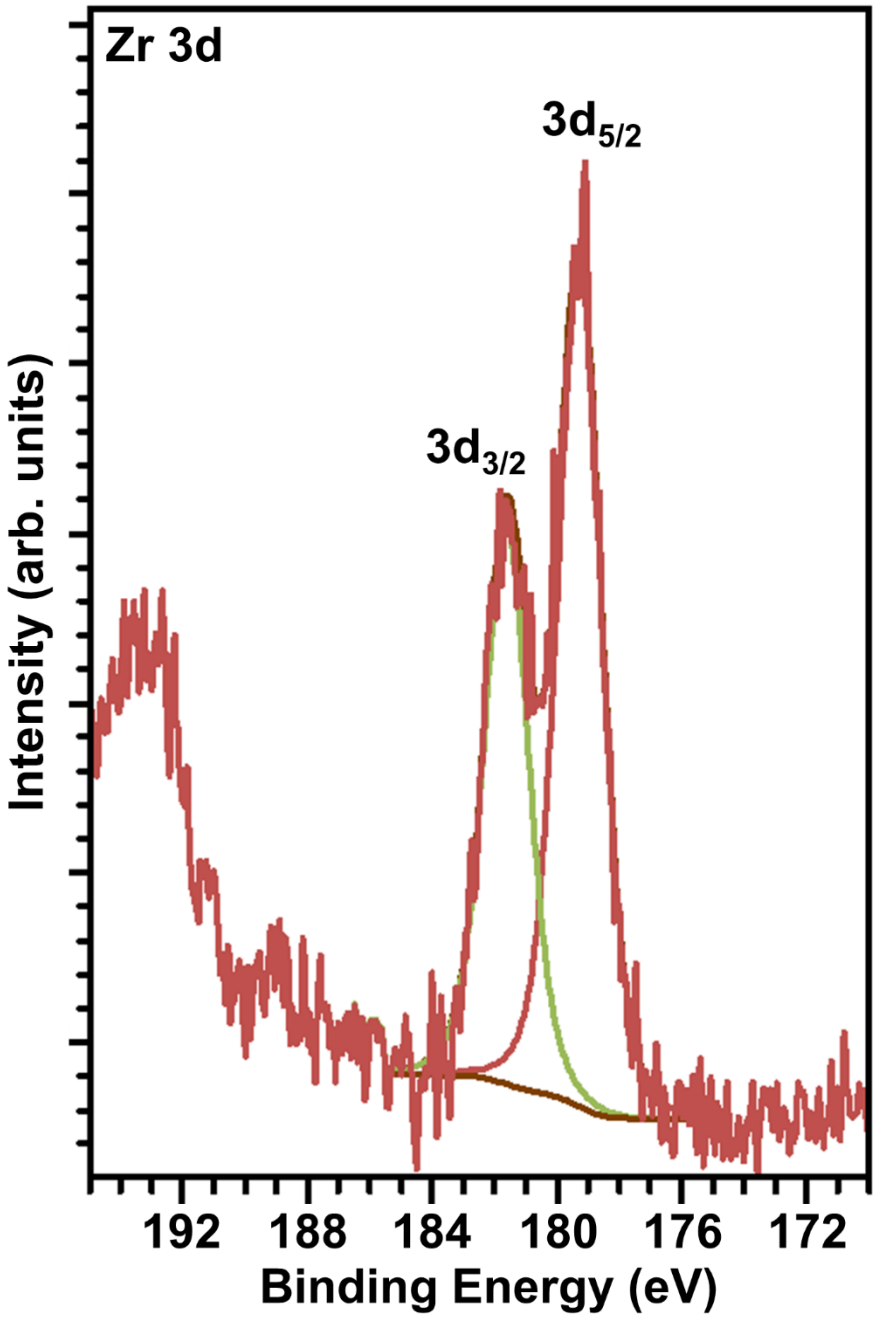

Figure 3. XPS spectrum of the Zr 3d peaks in undoped LLZO.

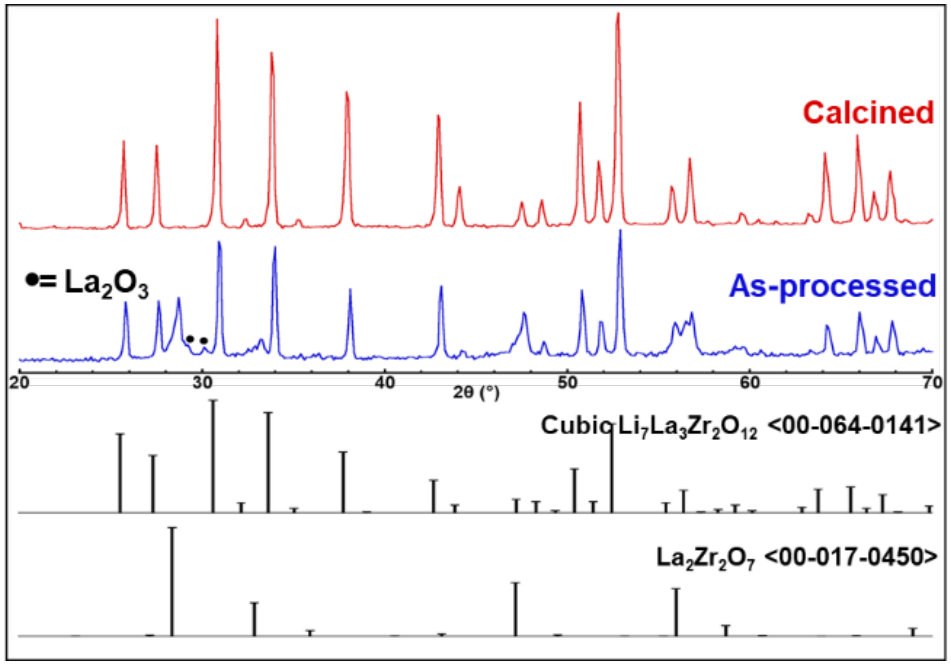

Figure 4. XRD patterns of as-processed and calcined (950°C/5 h) Ga-LLZO powders fabricated using SCS.

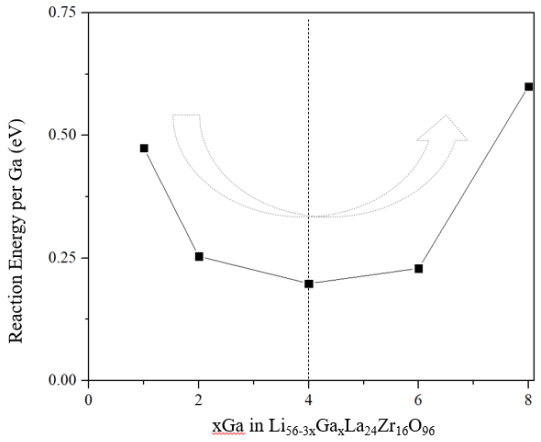

Figure 5. Stepwise reaction energy of $Li_{56-3x}Ga_xLa_{24}Zr_{16}O_{96}$ per Ga with respect to the xGa in LLZO. The reaction energy drops when xGa <=4, while it increased when xGa >=4.

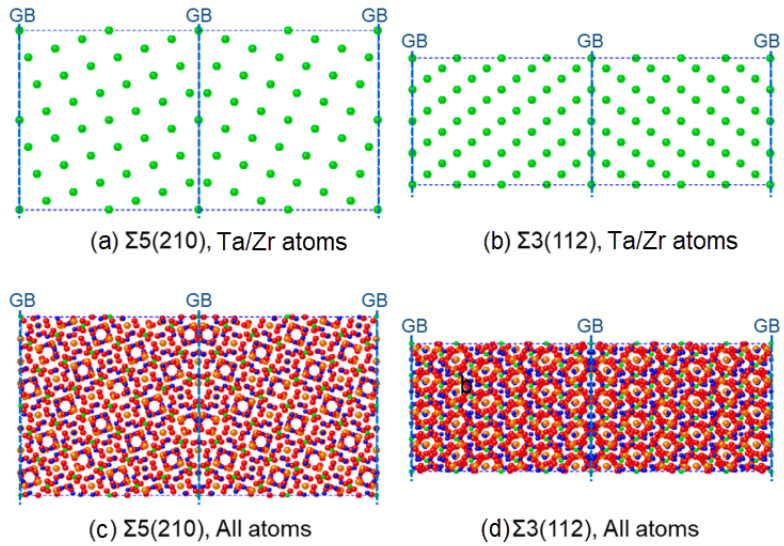

Figure 6. Unrelaxed structures of the two grain boundaries examined in Ta-doped LLZO.

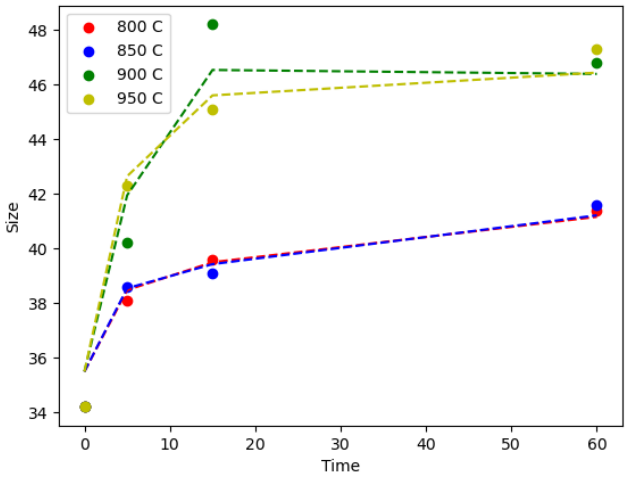

Figure 7. Plot of average crystallite size vs. sintering time showing experimentally measured data points (dots) and the preliminary results of model fit for the Random Forest regression model (dotted lines).

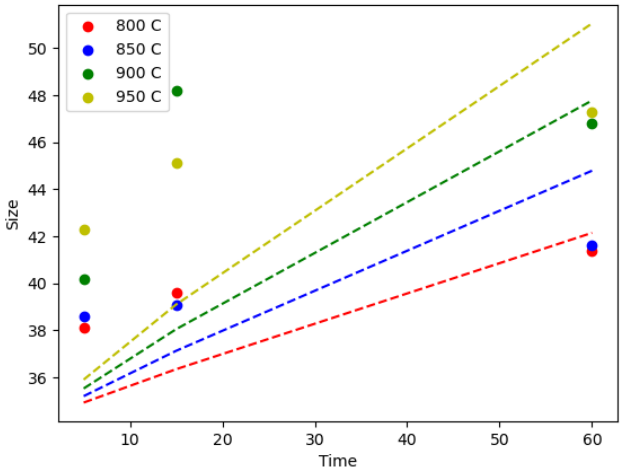

Figure 8. Plot of average crystallite size vs. sintering time showing experimentally measured data points (dots) and the preliminary results of model fit for the grain growth kinetics model (dotted lines).