The Effects of Microwave Irradiation on the Crystalline Structure and Ionic Conductivity of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP)

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Abstract

The goal of this research was to investigate the effects of microwave irradiation on the crystalline structure and ionic conductivity of Lithium Aluminum Germanium Phosphate (LAGP), a promising electrolyte for solid-state batteries. This research utilized electric, magnetic, and mixed fields in a microwave apparatus to expose LAGP samples to varying power levels and exposure times. Comparing these samples that have been microwaved to samples that have been thermally sintered at various temperatures helps to establish a baseline for how microwaves affect the microstructure. The grain structures of the samples were analyzed using a Scanning Electron Microscope (SEM) to identify correlations between field exposure and crystalline structure changes, specifically focusing on their impact on ionic conductivity. The expected outcome of this study was to gain insights into how microwave irradiation affects LAGP's crystalline structure and its subsequent influence on ionic conductivity. By understanding these relationships, the research attempted to contribute valuable information to the development of solid-state batteries based on LAGP, potentially leading to safer and more efficient energy storage solutions for electric vehicles and green energy applications.

1. Introduction

Batteries have been around since the 1800's and are composed of an electrolyte and 2 terminals. The positive terminal which is called the cathode, and the negative terminal known as the anode is separated by the electrolyte. [1] Traditional batteries have a liquid electrolyte between the anode and cathode. The electrolyte must be able to allow ions and electrons to flow through the substance with minimal resistance for maximum efficiency. Research has recently begun in the field of solid-state electrolyte batteries due to the energy density of the electrolytes. A much greater amount of energy can be stored in a battery of the same size if the electrolyte is in solid form. Solid-state batteries would also be safer in transport than a traditional lead-acid battery. It is for this reason that many researchers such as Zhang, et al. have begun exploring various NASICON (Sodium Superionic Conductor)-type electrolytes, such as LAGP (Lithium Aluminum Germanium Phosphate) [2]. Mahmoud, et al. [3] began studying the effects of microwaves on the activation energies and grain structures of LAGP. Yan, et al. [4] conducted research on microwave-assisted sintering to speed up the time-consuming and expensive process of sintering the LAGP pellets. Very little research has been done on the effects of microwaves on the grain structure and ionic conductivity of LAGP for use in solid-state batteries. By studying the changes that take place due to microwave processing, we hope to refine a quick and cost-effective process by which to optimize LAGP as a solid-state electrolyte. Using a microwave magnetron and a waveguide, we can isolate the fields of the microwaves to observe the different effects on the LAGP pellets in the E (Electric) field, the H (Magnetic) Field, and the M (Mixed) fields.

2. Method

To begin this research, LAGP powder was acquired (Ampcera™ $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ 99.99% pure, Particle size: (D50) 500nm) and prepared for microwave experimentation. Pellets were pressed into cylinders with dimensions of $\approx 6_{mm}$ diameter, $\approx 1.3_{mm}$ thickness, and a mass of $\approx .07_g$. These pressed pellets were then sintered at various temperature to study the effects of the thermal sintering. There were 4 main temperatures, PT (Pressed Thermal) were sintered at 800°C, PTB (Pressed Thermal B) were sintered at 450°C, PTL (Pressed Thermal Low) were sintered at 275°C, PTW (Pressed Thermal Warm) were sintered at 150°C, and CP (Cold Pressed) were

pressed at room temperature with no further processing. Each temperature sintered for a duration of 8 hours in a sintering furnace. Once the pellets were prepared, the pellets were measured and weighed for density calculations and labeled in an Excel™ spreadsheet for future reference. The labeled pellets could now be exposed to various electromagnetic fields for research on the effects. A single-mode microwave and a commercial CEM unit (Discover® SP CEM) were used to microwave the samples. Notes were taken in order to record the power and duration for each microwave run. They were then labeled according to the field used, adding an E to the label for electric field, an H for Magnetic field, an M for mixed field, and a C for the commercial CEM unit. After the samples had been microwaved, they were prepared for SEM (Scanning Electron Microscope) observation. In order to achieve more clarity in the SEM, the samples were painted with conductive silver paint on the bottom to avoid charge build-up during the observation. Once all data and pictures had been recorded for the samples, they were then prepared for EIS (Electrochemical Impedance Spectroscopy) by painting the top of the sample with the silver conductive paint and adding a gold contact to the top of the silver paint to ensure a good connection to the apparatus.

3. Results

We were able to successfully process and document 46 samples for SEM and EIS analysis. All of the samples mentioned were weighed and measured for density calculation, the microwave conditions were documented, and the effects categorized. A pattern of changes from the microwaves began to emerge from the data. Figure 1 shows the baseline SEM images that the subsequent images can be compared to.

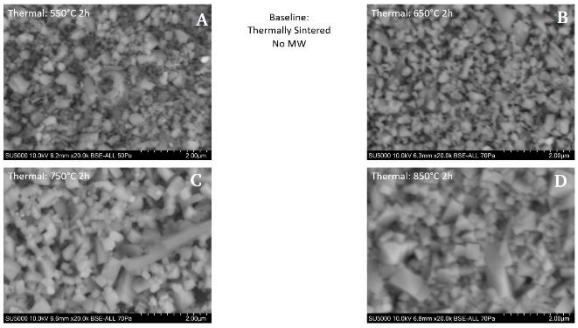

*Fig. 1: SEM images of **A.)** 550°C **B.)** 650°C **C.)** 750°C **D.)** 850°C*

A change in microstructure occurs from the 650°C sample to the 750°C sample. The crystal changes from smaller irregular particles to more uniform larger blocks. The change in density can be seen Table 1 below.

Table 1: Thermal series measurements.

Sample ID	Diameter (mm)	Thickness (mm)	Mass (g)	Density (% Theoretical)	Grain Size (nm)
PT550°	5.89	1.42	0.072	52.3%	270.55 ± 9.81
PT650°	5.84	1.35	0.067	52.0%	273.512 ± 11.57
PT750°	5.19	1.25	0.068	72.2%	266.40 ± 13.08
PT850°	4.84	1.06	0.065	93.6%	335.37 ± 12.90

One of the interesting characteristics that arose in the data was the formation of a network-like structure in the microstructure. Examples of this can be seen in Figure 2 below.

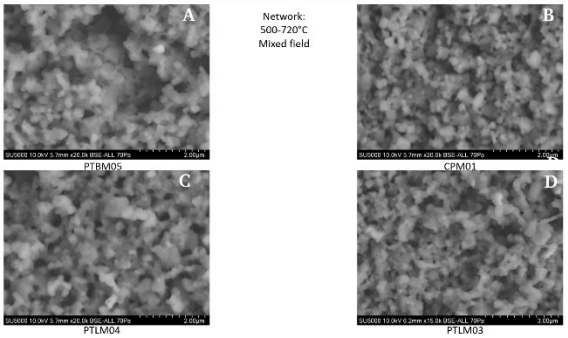

*Fig. 2: SEM images of **A.)** PTBM05 **B.)** CPM01 **C.)** PTLM04 **D.)** PTLM03*

This network formed in the mid-range temperatures of ≈500-720°C. It also primarily formed in the mixed field. Table 2 shows the measurements taken of the samples with the network structures. Sample CPM01 was broken during experimentation and has no density measurements.

Table 2: Network measurements.

Sample ID	Diameter (mm)	Thickness (mm)	Mass (g)	Density (% Theoretical)
PTBM05	5.87	1.40	0.068	50.4%
PTLM04	5.85	1.43	0.068	49.7%
PTLM03	5.87	1.49	0.070	48.8%
CPM01	n/a	n/a	n/a	n/a

All of these samples have a density of ≈50% of LAGP's theoretical density. During the research process, another interesting structure that was observed was the presence of nanowires forming on the crystal structure. These nanowires can be seen in Figure 3.

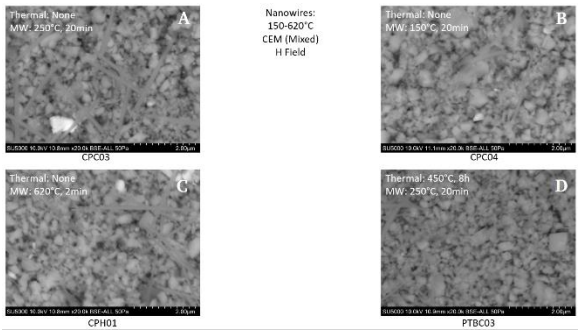

*Fig. 3: SEM images of **A.)** CPC03 **B.)** CPC04 **C.)** CPH01 **D.)** PTBC03*

These nanowires formed in mixed and magnetic fields. The temperature of these nanowire samples stayed lower in the range of ≈150-620°C. The corresponding measurements for the nanowire samples are in Table 3.

Table 3: Nanowire measurements.

Sample ID	Diameter (mm)	Thickness (mm)	Mass (g)	Density (% Theoretical)	Grain Sizes (nm)
CPC03	5.80	1.40	0.071	53.9%	273.63 ± 8.87
CPC04	5.86	1.25	0.068	56.7%	244.88 ± 10.60
CPH01	5.84	1.40	0.070	52.4%	241.63 ± 10.02
PTBC03	n/a	n/a	n/a	n/a	n/a

Each of these samples have been processed for EIS analysis, the data for this process is still being recorded and processed and is not available at the time of writing this paper.

4. Discussion

This research has brought to light the possibilities of microwave processing for improved conductivity and reduced time and cost for preparing the electrolyte for use. The correlations between microwave field, power, and duration have been demonstrated and are repeatable to form specific structures in the grains. The use of the microwave to sinter the LAGP in a fraction of the time as proposed by Lisenker and Stoldt [5] was confirmed. The sample PTWM02 was sintered at the lowest temperature of 150°C and microwaved for 2 minutes and reached a temperature of 800°C in Figure 4 these 2 samples structures are compared side-by-side.

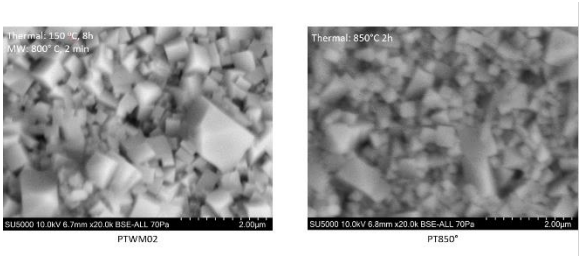

Figure 4: SEM Images of PTWM02 (left) and PT850° (right)

The same cubic structure is seen after only 2 minutes exposed to high levels of microwave radiation. The possibility of improved ionic conductivity in the network and nanowire structures would mean a large advancement in the usefulness of LAGP as a solid-state electrolyte. LAGP is a promising candidate for solid-state batteries, especially with the sinterablility in a short period of time with microwave processing. As explained by Wiemer, Schäfer, and Weitzel [6] the use of LAGP in batteries would make batteries safer and more reliable due to its electrochemical stability and low toxicity. Further advancements to complete this research would include the EIS data for these samples being analyzed, the Dielectric Constant being calculated, and doing research on the anode and cathode interface. With all of the components put together, a reliable and cost-effective battery could be achieved.

Acknowledgments

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