Microwave Processing of Solid-State Electrolyte for Li-Ion Batteries

M. M. Mahmoud[1,2,3*], Y. Cui[2], M. Rohde[2], C. Ziebert[2], G. Link[4], H. J. Seifert[2]**

[1] Mechanical Engineering Dep't, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

[2] Institute for Applied Materials—Applied Materials Physics (IAM-AWP), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen 76344, Germany.

[3] Fabrication Technology Dep't, Advanced Technology and New Materials Research Institute (ATNMRI), City of Scientific Research and Technological Application (SRTA), New Borg Al-Arab City, Alexandria 21934, Egypt.

[4] Institute for Pulsed Power and Microwave Technology (IHM), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen 76344, Germany.

Electrical energy storage systems have attracted a lot of attention in the past decades because of the urgent need and the development of alternative energy sources. New generations of energy storage systems with large battery modules that are needed for the future electrical grid should have higher safety standards. The development of clean and highly efficient energy storage systems is becoming an even more urgent goal. As an electrochemical energy storage device, rechargeable lithium-ion batteries have been the dominant power sources for portable electronic devices due to their high energy density. They are also being pursued intensively for automotive and stationary storage applications.

Solid-state electrolytes made of phosphate based ion conducting glass-ceramics are thermally more stable, non-flammable with higher melting points compared to the commercially used liquid and polymer based electrolytes. They also have good mechanical stability that could stop the dendrite growth which causes serious problems in some liquid electrolyte based batteries. Lithium aluminum-germanium phosphate glass-ceramics (LAGP: $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$) have a NaSICON (Sodium Super Ionic Conductor) structure. Lithium aluminum-germanium phosphate (LAGP) glass-ceramics are considered as promising solid-state electrolytes for Li-ion batteries.

LAGP glass was prepared via the regular conventional melt-quenching method. Thermal, chemical analyses and X-ray diffraction (XRD) were performed to characterize the prepared glass. The crystallization of the prepared LAGP glass was done using conventional heating and high-frequency microwave processing. A 30-GHz microwave (MW) processing setup was used to convert the prepared LAGP glass into glass-ceramics, as shown in Fig.1.

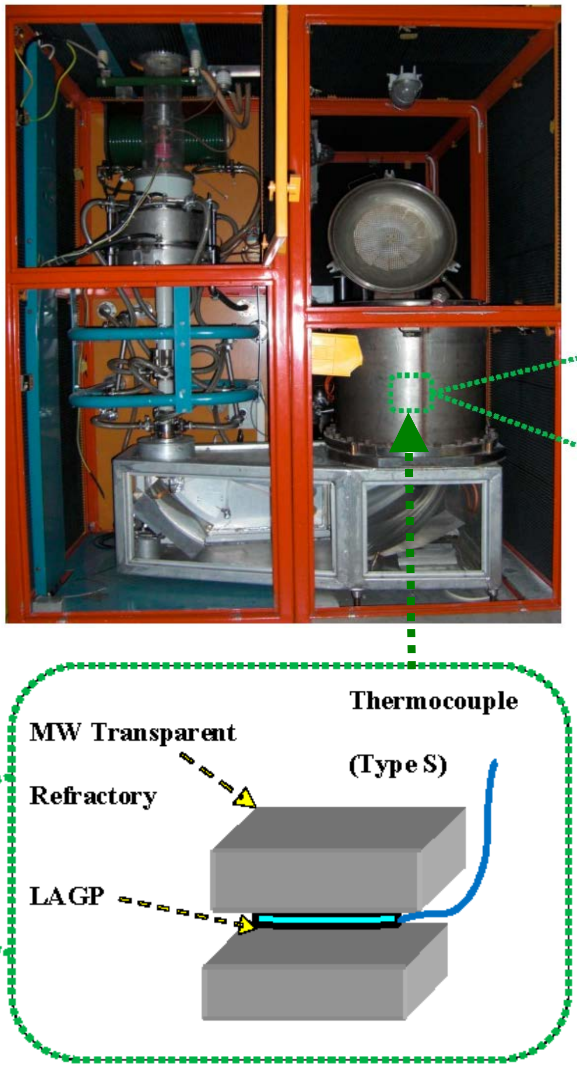


Figure 1. A 30-GHz microwave gyrotron system, and a schematic of the lithium aluminum-germanium phosphate (LAGP) glass crystallization setup.

The results were compared with conventionally crystallized LAGP glass-ceramics that were heat-treated in an electric conventional furnace. The ionic conductivities of the LAGP samples obtained from the two different routes were measured using impedance spectroscopy. These samples were also characterized using XRD and scanning electron microscopy (SEM).

A 30-GHz microwave processing was used successfully to crystallize lithium aluminum-germanium phosphate glass composition into ion-conducting glass-ceramic materials without the aid of hybrid heating. The ionic conductivities of the optimized heat-treated LAGP glass-ceramics samples at 800 °C for 6 h, using microwave and conventional heating, are shown in Fig. 2.

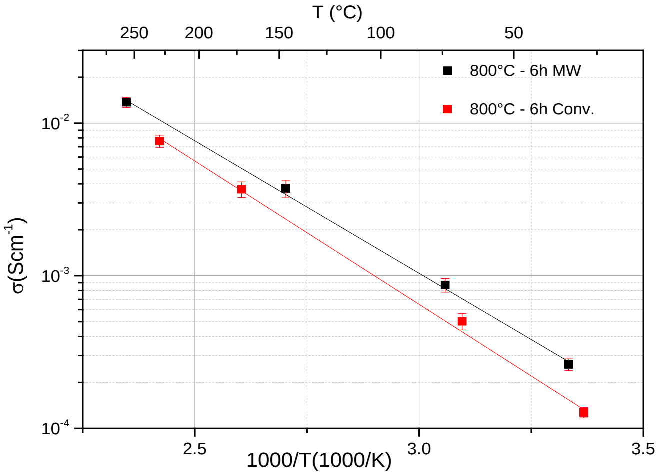


Figure 2. Ionic conductivity of LAGP glass-ceramics samples heat-treated at 800 °C for 6 h using 30-GHz microwave and conventional heating.

From the impedance measurements of both samples, the corresponding Nyquist diagrams at room temperature (RT) were derived, as shown in Fig. 3 along with the standard equivalent circuit model (ECM).

From both figures, it is concluded that the 30-GHz MW crystallized LAGP sample had higher total ionic conductivity at room temperature (2.77×10^{-4} S/cm) compared to the conventionally treated LAGP sample (1.3×10^{-4} S/m). This trend was also observed at higher temperatures. So, the MW crystallized samples at the optimum heat-treatment conditions exhibited *(i)* higher total ionic conductivity values over the measured temperature range with lower activation energy, *(ii)* relatively larger-grained microstructure with less porosity as shown in Figs. 4 and 5, as well as *(iii)* higher grains and grain boundaries conductivities when compared to the corresponding conventionally crystallized LAGP sample at the same conditions, as shown in Table 1 and 2.

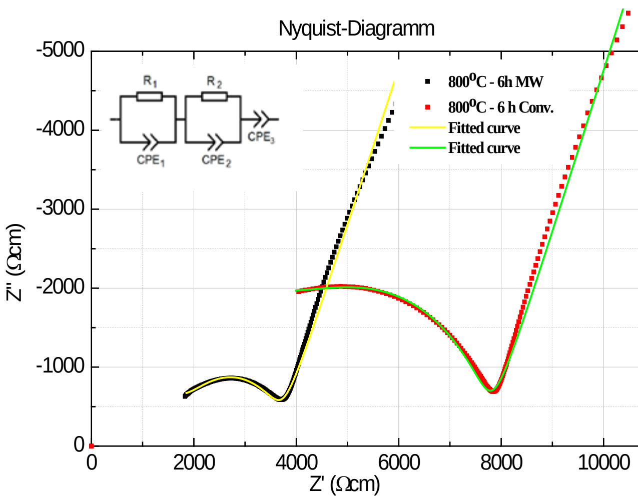


Figure 3. Impedance spectrum and equivalent circuit at room temperature (25 °C) of LAGP glass-ceramics samples heat-treated at 800 °C for 6 h using 30 GHz microwave and conventional heating.

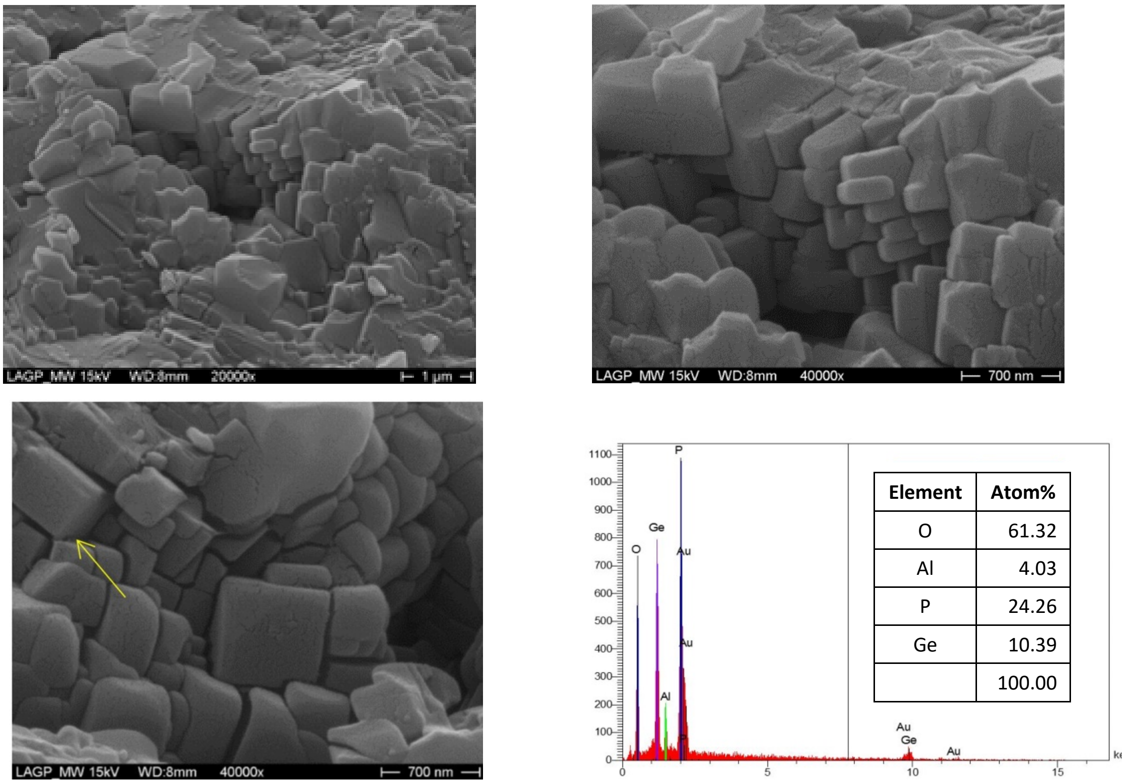
The enhanced ionic conductivity values (namely the total, grains and grain boundary ionic conductivities) along with the reduced activation energy that occurred in the MW treated samples was considered as another experimental strong evidence for the existence of the microwave effect in the LAGP crystallization process. Since microwaves can interact with materials via different types of conductions and polarizations losses, it is believed that microwaves interfacial (grain boundary) polarization and relaxation have contributed significantly to the observed enhanced grain boundary and total ionic conductivity values in the MW treated sample, as compared to the conventionally treated sample.

Microwave processing technology is an attractive tool which offers new opportunities and promising alternatives in the production of solid-state electrolyte for Li-ion batteries. It might lead to faster and greener LAGP production process, reduce its production cost, and save considerable amount of energy.

For further reading:

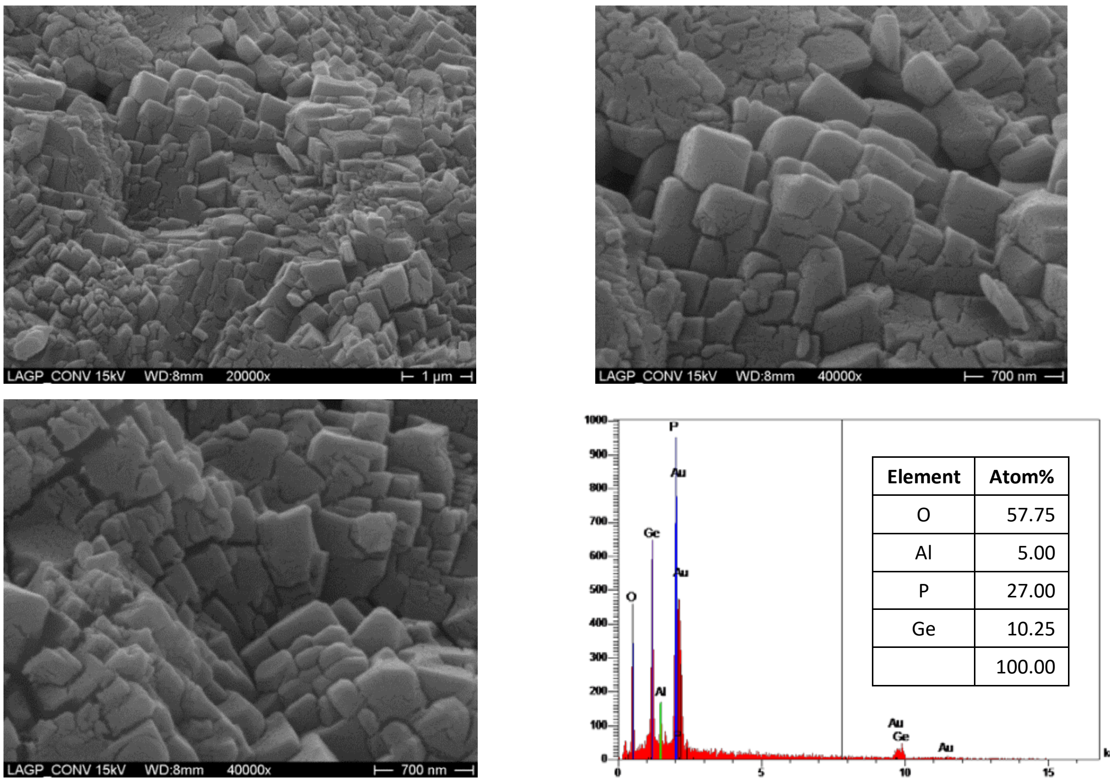
1. M. M. Mahmoud, Y. Cui, M. Rohde, C. Ziebert, G. Link, H. J. Seifert, "Microwave crystallization of lithium aluminum germanium phosphate solid-state electrolyte" *Materials* (MDPI Open Access), 9 (7), 506, 2016.

2. Morsi M. Mahmoud, Proc. 3rd Global Congress on Microwave Energy Applications (3GCEMA), Cartagena, Spain, July 25-29, 2016.



Element	Atom%
O	61.32
Al	4.03
P	24.26
Ge	10.39
	100.00

Figure 4. SEM micrographs with EDX data of LAGP glass-ceramics sample heat-treated at 800 °C for 6 h using 30-GHz microwave heating.



Element	Atom%
O	57.75
Al	5.00
P	27.00
Ge	10.25
	100.00

Figure 5. SEM micrographs with EDX data of LAGP glass-ceramics sample heat-treated at 800 °C for 6 h using conventional heating.

Table 1. Total, grains and grain boundaries ionic conductivities of the optimized conventionally and MW heated-treated LAGP samples at room temperature

Sample	Total Ionic Conductivity (S/cm) @ RT	Grains Ionic Conductivity (S/cm) @ RT	Grain Boundaries Ionic Conductivity (S/cm) @ RT
LAGP Conv. (800 °C/6 h)	1.3×10^{-4}	3.06×10^{-4}	2.25×10^{-4}
LAGP 30 GHz MW (800 °C/6 h)	2.77×10^{-4}	6.49×10^{-4}	4.83×10^{-4}

Table 2. Activation energies of optimized conventionally and MW heated-treated LAGP samples below and higher than 70 °C

Sample	Below 70 °C	Above 70 °C	Overall Range
LAGP Conv. (800 °C/6 h)	0.44 eV	0.34 eV	0.37 eV ± 0.010
LAGP 30 GHz MW (800 °C/6 h)	0.38 eV	0.32 eV	0.33 eV ± 0.008

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About the Corresponding Author

Morsi M. Mahmoud has recently joined the Mechanical Engineering Department at King Fahd University of Petroleum and Minerals, Dhahran, Kingdom of Saudi Arabia (KSA) since September 2016. He also holds an Associate Professor position in Advanced Technology and New Materials Research Institute (ATNMRI), City for Scientific Research and Technological Applications (SRTA City), Egypt. From December 2009 till August 2016, he was working as a Visiting Assistant Professor, then as a Senior Scientist at Karlsruhe Institute of Technology (KIT), Germany, at both Institute for Pulsed Power and Microwave Technology (IHM) and Institute of Applied Materials-Applied Materials Physics (IAM-AWP). Dr. Mahmoud has got his PhD degree in Materials Science and Engineering from Virginia Tech, Blacksburg, USA back in 2007. His research interest is related to advanced materials processing techniques such as microwaves and laser processing, structure-property-processing relationship in materials in addition to materials characterization techniques.

Dr. Mahmoud had been involved in editing several technical publications and organizing conferences, web-seminars and scientific events, such as he is serving as the chairman and the organizer of the “Microwave Processing of Materials” related symposium at Materials Science & Technology Conference and Exhibition (MS&T), USA.

Finally, he had served as a co-editor for 7 edited books and published 28 technical papers in the top 10 ISI ranked journals in Materials Science and Engineering. He had awarded several prestigious awards such as: Virginia Tech Citizen Scholar Award, an Honor Scholarship from Virginia Tech Graduate School, USA and Two German Academic Exchange Service (DAAD) Fellowships.

* E-mail: morsimahmoud@kfupm.edu.sa

** More about the microwave material processing group at KIT in Issue 88 of AMPERE Newsletter: http://www.ampereeurope.org/nwslttr/ampere_newsletter_88.pdf