



# Thermal and ionic conductivity studies of lithium aluminum germanium phosphate solid-state electrolyte



Yuantao Cui<sup>a</sup>, Morsi M. Mahmoud<sup>a,b,\*</sup>, Magnus Rohde<sup>a</sup>, Carlos Ziebert<sup>a</sup>, Hans Juergen Seifert<sup>a</sup>

<sup>a</sup> Institute for Applied Materials – Applied Materials Physics (IAM-AWP), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen 76344, Germany

<sup>b</sup> Advanced Technology and New Materials Research Institute (ATNMRI), City of Scientific Research and Technological Application (SRTA), New Borg Al-Arab City, 21934 Alexandria, Egypt

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## ABSTRACT

Two different compositions of lithium aluminum germanium phosphate glass–ceramics (LAGP) were prepared and investigated as candidate materials for solid-state electrolytes in Li-ion batteries. The thermal and the ionic conductivity behavior of these two different LAGP compositions were investigated. LAGP glasses were prepared using the melt-quench-method. Glass–ceramic samples were obtained from the prepared glasses via two different methods: powder sintering and bulk glass heat-treatment. The ionic conductivity was measured using complex impedance spectroscopy while the thermal diffusivity was measured using a Laser flash apparatus. The thermo-physical properties were studied using differential scanning calorimetry. X-ray diffraction and scanning electron microscopy were used to investigate the crystal structure and the microstructure. The sample with higher ionic conductivity had also shown higher thermal conductivity in the two different studied LAGP compositions. Moreover, the thermal conductivity was depending on the microstructure and density of the samples. Finally, the temperature dependence of the thermal conductivity could not be explained by a single mechanism or by the Wiedemann–Franz law. Therefore, a contribution of the mobile ions to the thermal transport might probably occur.

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## 1. Introduction

Ceramic solid electrolytes are key elements of all solid state batteries. It can be expected that they will replace the current liquid electrolytes which are considered nowadays as state of the art commercially. Liquid electrolytes can only operate in a restricted temperature window and therefore exhibit some safety risks such as degradation and inflammation [1,2]. Ceramic solid electrolytes are thermally very stable [3] and they are nonflammable with high melting points. Furthermore, they can easily operate at higher temperatures thereby reducing the safety risks due to uncontrolled thermal behavior in the cells and also gaining from the fact that the ionic conductivity increases with temperature to a level comparable with that of the liquid electrolyte.

Lithium aluminum germanium phosphate glass–ceramics (LAGP:  $\text{Li}_{1+x}\text{Al}_x\text{Ge}_2-x(\text{PO}_4)_3$ ) have a NaSICON (Sodium Super Ionic Conductor) structure consisting of two polyhedra [4–6], the  $\text{GeO}_6$ -octahedra and the  $\text{PO}_4$ -tetrahedra which are linked by their corners forming a 3D-skeleton with bottlenecks which are oriented along the *c*-axis through which the Li-ions can pass [7]. Doping of the parent structure  $\text{LiGe}_2(\text{PO}_4)_3$  by  $\text{Al}^{3+}$  ions introduces additional vacant lattice sites

which enhances the Li ion diffusion leading to higher ionic conductivity and lower activation energy. Compared to liquid electrolytes with conductivity values of the order of  $10^{-2}$  S/cm, the ionic conductivity of LAGP at room temperature is still relatively low and it is in the range between  $10^{-4}$  to  $10^{-3}$  S/cm [8–11]. However, this is compensated at elevated temperatures [10–12] where LAGP ionic conductivity can reach or exceed that in a liquid electrolyte. A further unique and important issue for the transport processes in ceramic electrolytes is the effect of the microstructure [13,14] since grain boundaries as well as arrangement and size of the grains can be adjusted by a proper heat treatment which affects the ionic and the thermal transport.

For the modern battery system, especially large battery modules, its temperature needs to be carefully monitored and controlled. The thermal properties of any battery such as heat capacity and thermal conductivity are essential for such application. Therefore, it is important to study the thermal conductivity of solid electrolytes. Hence, it is vital to evaluate the thermal conductivity of such promising LAGP electrolyte because this thermo-physical parameter mainly determines its thermal behavior. Since the thermal conductivity measurements also give information about the concentration of vacancies or interstitials within a certain material, it is of great interest to investigate whether there is a direct correlation between the thermal and the ionic conductivities in LAGP glass–ceramics. The heat transport properties in superionic conductors, namely the thermal conductivity and the thermal diffusivity, have been studied in a much fewer number of publications compared

\* Corresponding author at: Institute for Applied Materials – Applied Materials Physics (IAM-AWP), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen 76344, Germany.

E-mail address: [morsi.ahmed@kit.edu](mailto:morsi.ahmed@kit.edu) (M.M. Mahmoud).

**Table 1**  
Chemical composition of the prepared LAGP batches.

Type	Overall chemical formula
LAGP-1	$\text{Li}_{1.70}\text{Al}_{0.61}\text{Ge}_{1.35}\text{P}_{3.04}\text{O}_{12.0}$
LAGP-2	$\text{Li}_{1.31}\text{Al}_{0.42}\text{Ge}_{1.52}\text{P}_{3.09}\text{O}_{12.1}$

to the number of studies on ionic transport properties. Furthermore, these heat transport properties might give additional information about the physics of the conducting ions. Since these properties include the coupling between the heat flow and the temperature gradient, these thermal coefficients are very important for every system in which heat may flow, as in the case of solid electrolytes. Thermal conductivity measurements of some ionic conductors such as  $\text{Ag}^+$  Iodide [15],  $\beta$ -Alumina [16] as well as in  $\text{Li}_2\text{SO}_4$  and  $\text{NaPO}_4$  [17–21] were reported. On the other hand, only a few number of model approaches with regard to theoretical modeling and investigations to predict or to calculate the thermal conductivity were discussed [22–25]. One of the important issues was related to the possible contribution of the mobile ionic charges to the thermal transport in addition to the phonon transport in the absence of free electrons. This would also imply a correlation between thermal and ionic transport in such ionic conductors that would be somehow similar to Wiedemann–Franz law [26–28] for metal conductors with a large concentration of free electrons. This law implies that the ratio between the thermal and the electrical conductivity is proportional to temperature and therefore this ratio is constant at a fixed temperature. In a previous study on ion conducting composites, Chandra et al. [29,30] reported and found such a correlation when the weight fraction of the phases within the studied composite was varied.

In the present study, the thermal and the ionic conductivity behavior of two different composition LAGP samples were investigated.

## 2. Experimental work

LAGP glasses were prepared using a melt-quenching-route. Similar procedures were also employed in several studies [6,11].  $\text{Li}_2\text{CO}_3$  (Fluka, 99.0%),  $\text{Al}_2\text{O}_3$  (Sigma-Aldrich, 98.5%),  $\text{P}_2\text{O}_5$  (Analar Normapur, 99.1%) and  $\text{GeO}_2$  (Alfa Aesar, 99.98%) were used as starting materials. The mixture of these powders was heated up to 1450 °C using a heating rate of 5 °C/min in an  $\text{Al}_2\text{O}_3$  crucible and held at that temperature for 10 min. The melt was then quenched on a steel plate at room temperature and pressed with another steel plate immediately to form a thin glass disc. Then, the prepared glasses had been converted into glass-ceramics materials via two different routes: the powder sintering route or the heat treatment route of the bulk glass, respectively. For the powder preparation, the thin glass discs were ground into powder using a ball mill. After green compaction in an isostatic press, the pellets were sintered in air applying sintering temperatures up to 800 °C and holding times up to 6 h. The bulk glass pieces were annealed at 500 °C for 1 h to remove the thermal stresses and then subsequently heat treated at temperature levels up to 800 °C in order to transform the glass into a glass-ceramic.

The chemical composition of the prepared glass was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 4300 DV, Perkin-Elmer). The oxygen content was measured using Carrier Gas Hot Extraction (CGHE, TC 600, Leco Co.). The glass transition temperature ( $T_g$ ) and the crystallization temperature ( $T_x$ ) were determined using differential scanning calorimeter (DSC 404, Netzsch).

The microstructure of the prepared glass-ceramics samples was examined using scanning electron microscopy (SEM) on the fractured and polished surfaces whereas energy-dispersive X-ray spectroscopy (EDX) measurements were also carried out (FEI XL30S, PHILIPS). The developed crystalline phases in these samples were identified using X-ray

diffraction (SEIFERT XRD 3003 PTS) with  $\text{Cu K}\alpha$  radiation. The density of the samples was measured with the Archimedes method.

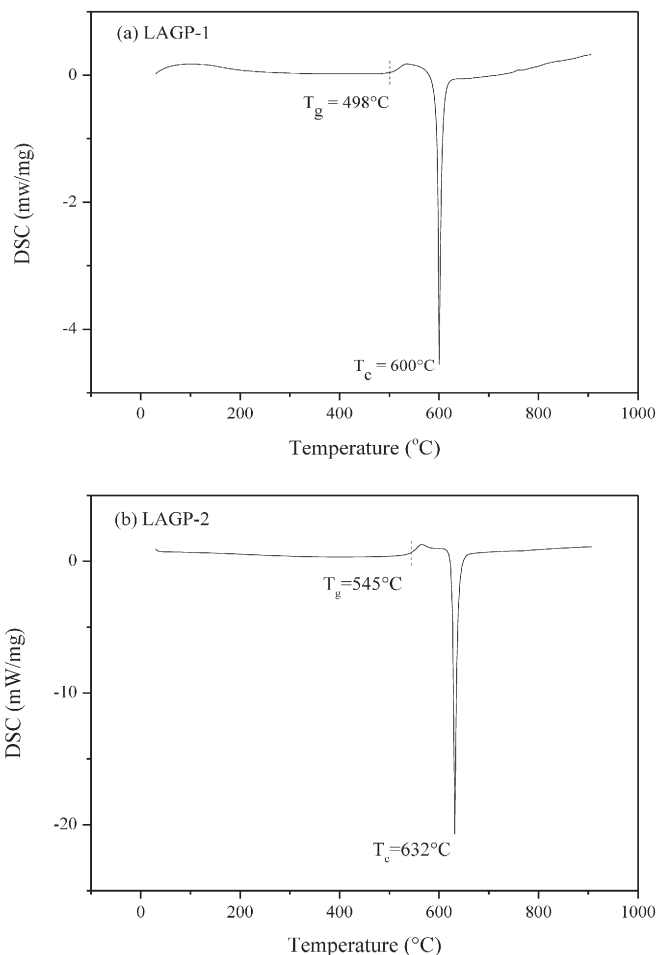
The ionic conductivity of the glass-ceramics samples was measured using impedance spectroscopy (Sourcetric 2826). The principles of these measurements were explained elsewhere [31,32]. Gold electrodes were sputtered on both sides of the samples before they were fixed between two current collectors and the whole assembly was inserted into a furnace with two cables connected to the analyzer outside. The ionic conductivity was measured from room temperature up to 250 °C.

For the determination of the thermal diffusivity, a commercial Laser flash apparatus (LFA 427, Netzsch) was used. The specific heat was measured using a differential scanning calorimeter (DSC 404, Netzsch). Using the common approach by multiplying the thermal diffusivity value with the specific heat and the density values, the thermal conductivity was calculated.

## 3. Results and discussion

The chemical composition of the two different prepared LAGP batches are shown in Table 1. Batch 1 was used for the powder sintering route whereas the second batch undergoes the heat treatment procedure of the bulk glass samples.

The DSC measurement technique was applied to determine the glass transition and the crystallization kinetics. The corresponding DSC traces for both LAGP batches are shown in Fig. 1a and b. Both traces are exhibiting similar characteristics during the heating process but with a



**Fig. 1.** DSC traces of LAGP-1 (a) and LAGP-2 (b) samples.

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