Glass-ceramics based on Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ for advanced all-solid-state batteries

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Abstract. Glass-ceramic electrolytes of the Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$-xB$_2$O$_3$ series (0≤x≤0.15 wt%) were obtained by glass crystallization under the same conditions of heat treatment. The influence of B$_2$O$_3$ addition on the phase composition and unit cell parameters of lithium-aluminium-germanium-phosphate glass-ceramics was investigated by XRD. The obtained solid electrolytes have the NASICON-type structure with space group R-3c. Glass-ceramics is single-phase at 0≤x≤0.15. Transport properties of glass-ceramics electrolytes were investigated by impedance spectroscopy. The conductivity of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ was found to be lower compared to the B$_2$O$_3$-added solid electrolytes. Namely, the composition with 0.05 wt% has the highest lithium-ion conductivity, which is 5.5·10$^{-4}$ S/cm at 25 °C. Also the thermal compatibility of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ solid electrolyte with Li$_4$Ti$_3$O$_{12}$ anode material and the influence of Li$_3$BO$_3$ addition on their compatibility were investigated by DSC method.

1. Introduction

Lithium-ion batteries with liquid electrolyte are widely used in various applications [1-4]. However, they still have disadvantages related to safety and volume energy density. The development of all-solid-state batteries with a solid electrolyte will improve safety and increase volume energy density of power sources by avoiding the irreversible loss of capacity on the initial charge [4]. To create attractive commercial all-solid-state batteries, it is necessary to solve the problems associated with the low Li-ion conductivity of solid electrolytes compared to liquid electrolytes (~10$^{-2}$ at room temperature), and a high interface resistance between solid electrolyte and solid electrodes [5].

One of the ways to increase the Li-ion conductivity of solid electrolytes is the introduction of sintering additives such as Li$_3$PO$_4$ [6], Li$_3$BO$_3$ [6], LiBO$_2$ [7], B$_2$O$_3$ [4, 8] or glassy additives with low melting points – LiPO$_3$ [9], Li$_2$O·B$_2$O$_3$–SiO$_2$ and Li$_2$O–Y$_2$O$_3$–SiO$_2$ [10], which leads to the compaction of ceramic materials at lower temperatures by liquid-phase sintering. Besides, the interfacial contact between the electrodes and electrolyte can be improved by lithium salts, in particular Li$_3$BO$_3$ [11].

Glass-ceramics based on Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP for short) is promising solid electrolytes due to the higher lithium-ion conductivity >10$^{-4}$ S/cm at 25 °C [4, 12], low porosity, grain uniformity and compact microstructure compared to sintered polycrystalline ceramics of similar composition and other oxide conductors [13]. B. Yan et al. [14] studied the effectiveness of dopants such as B, Ga, and In on the conductivity of LAGP glass-ceramics. It was found that the partial substitution of Al$^{3+}$ ion for B$^{3+}$ increases the grain boundary conductivity, in contrast doping with Ga$^{3+}$ leads to bulk
conductivity improvement, and co-doping with $B^{3+}$ and $Ga^{3+}$ increases total conductivity of initial compounds. The conductivity of LAGP glass-ceramics can be increased from $1.22 \times 10^{-4}$ to $6.9 \times 10^{-4}$ S/cm at 25 °C by introducing of 0.05 wt% $B_2O_3$ as reported in [15]. However, obtained glass-ceramics samples (with and without the $B_2O_3$ addition) were not single-phase, and an impurity phases in electrolytes such as $Li_2O$ and $AlPO_4$ were determined.

It is necessary to evaluate the thermal compatibility of LAGP glass-ceramics with electrode materials for its potential application as solid electrolyte. Lithium titanate ($Li_3Ti_5O_{12}$) is considered as the promising anode material for all-solid-state lithium-ion batteries due to its high theoretical capacity – 175 mA·h/g, low degradation during cycling, small change in the unit cell volume during intercalation / deintercalation of $Li^+$ ions [16, 17]. It can be assumed that $Li_3Ti_5O_{12}$ does not degrade during battery operation, unlike other anode materials (amorphous silicon, carbon / graphite, metallic lithium and its alloys).

We optimized the crystallization parameters of LAGP glass-ceramics in our earlier works [18, 19] and found that the most highly lithium-ion conductive electrolytes are obtained under the following crystallization conditions:
- annealing at 820 °C;
- heating time - 2 h;
- heating rate - 3 °C/min.

The purpose of this work is to optimize the transport properties of LAGP glass-ceramics by introducing of $B_2O_3$, as well as to study the thermal compatibility of LAGP with $Li_3Ti_5O_{12}$ (with and without the $Li_3BO_3$ addition) for potential use in all-solid-state lithium-ion batteries.

2. Materials and research methods

Glass-ceramics of $Li_xAl_{0.5}Ge_1.5(PO_4)_3-xB_2O_3$ (x=0, 0.05, 0.10, and 0.15 wt%) composition were obtained via glass crystallization method, using precursors of $Li_2CO_3$ (>99.4%), $Al_2O_3$ (>99.9%), $H_3BO_3$ (>99.9%), $GeO_2$ (>99.9%) and $NH_4H_2PO_4$ (≥98.0%). The mixture was heated to 1250 °C for 1 h in a Pt crucible. The melt was quenched between preheated steel plates. The samples of glasses were annealed at 500 °C, and then crystallized at 820 °C for 2 h.

$Li_3Ti_5O_{12}$ was synthesized by sol-gel method through the hydrolysis of tetraethoxytitanium, as described in [20]. The white precipitate of metatitanic acid was dissolved in $HNO_3$ (1:1) and a solution of $Li_2CO_3$ with citric acid was added. As a result, a clear solution was obtained, which was heated to form a gel at 80 °C for 12 h. Then the gel was heated at 200 °C and 500 °C in air. The resulting mixture was annealed at 800 °C for 5 h.

$Li_3BO_3$ was synthesized by melt quenching method, using precursors such as $Li_2CO_3$ and $H_3BO_3$. The mixture was heated to 1100 °C for 0.5 h in the Pt crucible.

The phase composition and lattice parameters of the glass-ceramics were determined by X-ray diffraction method (XRD) with a Rigaku D/MAX-2200VL/PC diffractometer over a 20 range of 10–60° with steps of 0.02° at room temperature. The collected data were processed with the FULLPROF program.

The thermal behavior of LAGP, $Li_3Ti_5O_{12}$, $Li_3BO_3$ powders, as well as a mixture of LAGP:$Li_3Ti_5O_{12}=1:1$ and LAGP:$Li_3Ti_5O_{12}:Li_3BO_3=1:1:1$ (mass ratio) powders was studied by DSC on a thermal analyzer Netzsch STA 449 F1 Jupiter. The measurements were carried out in Pt crucibles at the rate of 10 °C/min over a 35-800 °C temperature range at the expulsion rate of 20 mL/min in air atmosphere. Data analysis performed on the Netzsch Proteus software.

The electrical resistance of the samples was measured by the electrochemical impedance method in a two-probe cell with silver metal electrodes over the frequency range of 0.025–1000 kHz in air using potentiostat/galvanostat Ellins P-5X. The impedance spectra were obtained over a 25–150 °C temperature range. The samples were coated with Ga–Ag paste to form electrodes.
3. Results and discussion
To reduce the amount of microvoids and cracks in the LAGP glass-ceramics electrolyte, we used the addition of a sealing agent, namely boron oxide.

3.1. X-ray diffraction
Figure 1 shows X-ray diffraction patterns of LAGP–xB2O3 glass-ceramics as a function of B2O3 content. All diffractions peaks were well matched with the standard peaks of LAGP phase with a hexagonal structure, space group R-3c (LiGe2(PO4)3, JCPDS 80-1924). According to XRD data, compositions at 0≤x≤0.15 are single-phase.

![XRD results for the Li1.5Al0.5Ge1.5(PO4)3–xB2O3 glass-ceramics.](image)

The parameters and volume of the NASICON-type unit cell for the obtained samples with various compositions are given in Figure 2. It should be noted that the lattice parameters a and c depend on the composition of electrolyte, passing through the maximum value at x=0.10 (Figure 2a, b). Thereby, B3+ ions are incorporated into the LAGP structure and are responsible for the expansion of the unit cell, which correlates with the change in its volume (Figure 2c). It was assumed in work [15] that the B2O3 additive segregated in the grain boundaries. We have shown that B2O3 addition leads to the structural changes of the solid electrolyte.

![Unit cell parameters (a, b) and volume (c) of the LAGP–xB2O3 glass-ceramic samples.](image)

3.2. Transport properties of glass-ceramics
The electrical conductivity of the samples was measured using impedance spectroscopy. The total conductivity of solid electrolytes was found, as shown in our previous work [18], and temperature dependences of conductivity were plotted (Figure 3). The activation energy of conductivity (Ea) was
calculated according to the Arrhenius equation. It was found that the total conductivity of glass-ceramic electrolytes at 25 °C increases from \(5.0 \times 10^{-4}\) to \(5.5 \times 10^{-4}\) S/cm with the increase in the \(x\) content from 0 to 0.05, respectively. At \(x \geq 0.10\) the conductivity decreases. \(E_a\) decreases insignificantly from 35.4 (\(x=0\)) to 34.0 kJ/mol (\(x=0.15\)). The improvement of the transport properties of glass-ceramics with the small fraction of \(\text{B}_2\text{O}_3\) addition is associated with the expansion of channels for \(\text{Li}^+\) ions migration due to the increase of the unit cell volume, which was established in Section 3.1.

![Figure 3. Arrhenius plots for the total conductivity of the LAGP-\(x\text{B}_2\text{O}_3\).](image)

### 3.3. Evaluation of the thermal compatibility of LAGP with \(\text{Li}_4\text{Ti}_5\text{O}_{12}\)

It is necessary to know the temperature range in which the materials do not interact for determination the conditions at which the anode material can be sintering with the solid electrolyte. For this purpose, DSC-curves of individual materials (fresh-prepared LAGP and \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) powders), as well as their mixtures, were obtained (Figure 4). DSC-curves of both LAGP and \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) show no peaks up to 800 °C. However, on the DSC-curve of their mixture, intense exothermic peaks appear at 622, 676, and 783 °C, as well as the endothermic peak at 750 °C. Thus, the interaction of the components begins at temperatures above 550 °C (onset of the 1st peak). The obtained results agree with the literature data [21]; it was found that phase composition of the LAGP and \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) mixture changes by sintered at 700 °C for 1 h. The impurity phases of \(\text{TiO}_2\) and \(\text{Li}_3\text{PO}_4\) were detected [21].

![Figure 4. The DSC-curves for different materials at 10 °C/min.](image)
3.3.1. Influence of Li$_3$BO$_3$ on the thermal compatibility of LAGP with Li$_7$Ti$_3$O$_{12}$. The effect of the lithium borate addition on the thermal behavior of the electrolyte and anode material mixture was studied by DSC method (Figure 4). Exothermic peaks appear on the DSC-curve at 607, 637, 681 and 777 °C. The first exothermic peak was found to begin at 569 °C. Thus, the addition of Li$_3$BO$_3$ increases the thermal stability of the studied mixture (LAGP and Li$_7$Ti$_3$O$_{12}$) from 550 to 569 °C.

4. Conclusions
Glass-ceramics electrolytes of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$–xB$_2$O$_3$ (0≤x≤0.15 wt%) composition were obtained at 820 °C for 2 h. The phase composition of solid electrolytes did not change at x≤0.15. The lattice parameters a and c were shown to depend on the composition. The total conductivity of glass-ceramics correlates with the change of the unit cell volume and passes through the maximum at x≈0.05. The LAGP-0.05B$_2$O$_3$ glass-ceramics have the highest ionic conductivity of 0.55 mS/cm at room temperature. It was found that Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ and Li$_7$Ti$_3$O$_{12}$ do not interact up to 550 °C. The addition of Li$_3$BO$_3$ increases the thermal stability of the anode and electrolyte materials from 550 to 569 °C.

5. References
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