Production of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ ionic conductor from liquid-phase precursors

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Abstract. The synthesis of lithium-conducting solid electrolyte Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) from liquid-phase precursors using available water-soluble salts (LiNO$_3$, Al(NO$_3$)$_3$, (NH$_4$)$_2$HPO$_4$) and a stable citrate [Ge(C$_6$H$_5$O$_7$)$_3$]$^5-$ or oxalate [Ge(C$_2$O$_4$)$_3$]$^{2-}$ germanium complex was studied. Germanium complexes were obtained by dissolving the hexagonal modification of GeO$_2$ in citric or oxalic acid. As a result of the transfer of all initial components to the solution with the formation of a true collective solution, the subsequent interaction proceeded with the formation of a single-phase LAGP product in one stage from an oxalate precursor at 650°C, from a citrate precursor — at 800°C. The synthesized LAGP was studied by XRD, TG-DSC, IR spectroscopy, chemical analysis and impedance spectroscopy. The total ionic conductivity at room temperature was $8 \times 10^{-4}$ S/cm and $2.5 \times 10^{-4}$ S/cm for LAGP synthesized from oxalate and citrate precursor respectively. LAGP synthesis from oxalate precursor is preferred over synthesis from citrate precursor.

1. Introduction

Complex phosphates Li$_{1+x}$Al$_x$M$^{IV}_2-x$(PO$_4$)$_3$ (where M$^{IV} =$ Ti or Ge) with the structure of NASICON due to high conductivity in the ion Li$^+$, the chemical and thermal resistance, stability in air are promising for use in solid-state lithium-ion batteries, as gas-tight membranes in lithium-air cells and lithium-sulfur power sources [1-5]. Areas of application of solid electrolytes with NASICON structure are constantly expanding; there are reports of their use in the creation of nanostructured supercapacitors [6].

Currently, there are various methods for producing ion conductor Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$; solid-phase sintering, melt-quenching, sol-gel method [7-9]. Particular attention should be paid to the methods of Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ ion conductor synthesis from liquid-phase precursors which provide a single-phase target product as well as a significant reduction in temperature and duration of the process. The disadvantage of the known sol-gel methods is the use of expensive germanium and aluminum alkoxides which require precautions by processing in air due to their high sensitivity to moisture and the possibility of hydrolysis [9]. In this regard, there are publications that suggest methods for the synthesis of Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ using inorganic precursors of germanium [10-12]. Moshareva M.A. et al. [10] dissolved GeO$_2$ in an aqueous ammonia solution with a concentration of 1.2 wt.%. When combining this alkaline solution with other components due to changes in pH, the formation of sol was observed. For the formation of the rhombohedral NASICON structure Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ was required sintering temperature above 700°C and prolonged exposure (12 h). After sintering at 700°C...
on X-ray diffractograms were present GeO$_2$, GeP$_2$O$_7$ and Li$_4$P$_2$O$_7$ impurity phase. Conductivity values ($2 \times 10^{-4}$ S/cm) were determined by extrapolation of temperature dependence on room temperature. Sun et al. [12] recently reported a new sol-gel method for the Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ synthesis. Germanium oxide GeO$_2$ was dissolved in 25% NH$_4$OH solution at 60°C and combined with solutions of Li$_2$CO$_3$, Al(NO$_3$)$_3$·9H$_2$O and NH$_4$H$_2$PO$_4$ in citric acid. Formation of the gel occurred for a long time (24 h at 170°C) as a result of evaporation of solvents and polymerization between ethylene glycol and citric acid. Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ powder was obtained after gel calcination at 800°C for 5 h. Ion conductivity of the samples was $4 \times 10^{-4}$ S/cm (pellet density was not mentioned). Previously Kunshina et al. [13, 14] developed a new and extremely effective liquid-phase method for Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) synthesis from oxalate precursor with total ionic conductivity at $8 \times 10^{-4}$ S/cm. As is known, GeO$_2$ is also dissolved in a concentrated solution of citric acid to form H$_5$[Ge(C$_6$H$_5$O$_7$)$_3$] complex [15].

The aim of this work was to study the synthesis of LAGP solid electrolyte using germanium citrate complex and comparison with the LAGP synthesis using oxalate complex.

2. Experimental methods

The LAGP powders prepared from liquid-phase precursors were characterized by X-ray diffraction, differential scanning calorimetry, thermogravimetry (DSC/TG), and impedance spectroscopy. The phase composition of the powders was determined using a DRON-2 X-ray diffractometer (Cu K$_\alpha$-radiation, graphite monochromator). Thermal analysis was carried out with a Netzsch STA 409 PC/PG simultaneous thermal analyzer in the range 25-1200°C. IR spectra in the frequency range of 400 - 3800 cm$^{-1}$ were recorded on a Nicolet 6700 IR Fourierspectrometer. The ionic conductivity of LAGP synthesized powders studied by impedance spectroscopy method in the frequency range 10 to 2·10$^6$ Hz with the amplitude of alternating signal up to 100 mV. The measurements were performed under the two-electrode schema by Elins Z-2000 impedance meter. The samples for the measurements prepared in the form of pressed cylindrical pellets ($d = 1.2$ cm, $h = 0.1-0.2$ cm) on the end faces of which, after sintering at 900°C for 5 h, graphite electrodes were applied. The specific total ionic conductivity we calculated with consideration for the geometrical dimensions of the pellet

$$\sigma = \frac{h}{SR}$$

where $h$ is the thickness of the pellet, $S$ is the end surface area, and $R$ is the resistance of the pellet evaluated from the complex impedance plot.

As the initial substances we used LiNO$_3$·3H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, (NH$_4$)$_2$HPO$_4$ and water-soluble Ge citrate complex which was obtained by dissolving GeO$_2$ hexagonal modification in citric acid C$_6$H$_8$O$_7$·H$_2$O:

$$\text{GeO}_2 + 3 \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} = \text{H}_5[\text{Ge}(\text{C}_6\text{H}_5\text{O}_7)_3] + 5 \text{H}_2\text{O}$$

To the citrate solution of H$_5$[Ge(C$_6$H$_5$O$_7$)$_3$] (concentration 40-50 g/L according to GeO$_2$, density 1.1 g/cm$^3$, pH 0.3) aqueous solutions of lithium nitrates, aluminum nitrates and ammonium hydroxide in this sequence were added with stirring in accordance with stoichiometry. pH was 1.83 at the formation of a transparent collective solution. This solution was heated to 60-70°C at stirring for 4 h and was received a transparent viscous gel. Then the gel was heated at 300°C to form a black crystalline mass. Further increase to 700°C led to the burning of carbon to form a fine powder of dark gray color, obviously due to the high carbon content in the mixture.

3. Results and discussion

According to the results of XRD, it was found that in the samples there is an impurity of GeP$_2$O$_7$ (ICDD No. 82-0829) and AlPO$_4$ (ICDD No. 72-1161) (figure 1a) after sintering the powder at 700°C for 1 h using the germanium citrate complex. Single-phase LAGP (ICDD No. 80-1924) which does not contain non-conductive impurities is formed after sintering the powder at 800°C for 1 h. The
results of DTA and XRD show that the minimum sintering temperature for the formation of the pure LAGP phase is 800°C, the duration of 1 h. It should be noted that the formation of a single-phase LAGP occurs at a lower temperature 600-650°C, using the germanium oxalate complex \([\text{Ge(C}_2\text{O}_4)_3]^{2–}\) (figure 1b). This is obviously due to the fact that the thermal decomposition of the germanium oxalate complex with the formation of x-ray amorphous GeO₂ ends at 270°C and provides the interaction of the active components of the solid electrolyte at a low temperature [14], and the thermal decomposition of the citrate complex \([\text{Ge(C}_6\text{H}_5\text{O}_7)_3]^{5–}\) occurs stepwise at a higher temperature as established by the results of the IR spectra (figure 2).

![XRD patterns of LAGP citrate precursor (a) sintered at 400°C (1), 700°C (2) and 800°C (3) and LAGP oxalate precursor (b) sintered at 400°C (1) and 650°C (2).](image)

**Figure 1.** XRD patterns of LAGP citrate precursor (a) sintered at 400°C (1), 700°C (2) and 800°C (3) and LAGP oxalate precursor (b) sintered at 400°C (1) and 650°C (2).

Figure 2 shows the IR spectra of LAGP precursors obtained from citrate solutions after evaporation and calcination at 300°C, 400°C and 700°C (1-3) and the spectrum of citric acid (4). In the spectrum of LAGP precursor calcined at 300°C, the valence bands of OH– groups of citric acid (3289, 3448, 3493 cm⁻¹) disappear and appear \(\nu_{\text{OH H}_2\text{O}}\) (3422 cm⁻¹). With increasing temperature, the intensity of this band decreases and there is a low-intensity absorption band \(\nu_{\text{OH H}_2\text{O}}\) at 3422 cm⁻¹, possibly sorbed water, at 700°C. In the absorption region of the carbonyl group after calcination of LAGP precursors at 300°C, the absorption band disappears at 1753 cm⁻¹ and the band of 1704 cm⁻¹ becomes less intense. The intensity of this band decreases at 400°C and completely disappears at 700°C (figure 2) which may indicate the complete decomposition of germanium citrate complex.

Figure 3 shows the hodograph of the impedance of the cell C/LAGP/C at 20°C in the range \(10^3\)–\(2\cdot10^6\) Hz. The dependence \(Z'' = \phi(Z')\) on the complex plane is two weakly resolved semicircles corresponding to impedance measurements at high and medium frequencies, and a straight line
corresponding to impedance measurements at low frequencies. The values of the active resistance are determined by the points of intersection of the arc of the semicircle with the axis of the abscissa.

![Figure 2](image1.jpg)

**Figure 2.** IR spectra of the LAGP precursor obtained from citrate solution after heating at 300°C (1), 400°C (2) and 700°C (3) as well as the IR-spectrum of citric acid (4).

![Figure 3](image2.jpg)

**Figure 3.** Hodograph of LAGP impedance and corresponding equivalent electric circuit (numbers indicate frequency in Hz).

When the relaxation times of the charges in the grain volume and at the grain boundaries of the polycrystalline electrolyte differ slightly, the overlap of the arcs is observed on the impedance spectrum, which significantly complicates its analysis. The relaxation times of the charges in the grain volume and at the grain boundaries of LAGP calculated from the ratio:
\[ \tau = \frac{1}{2\pi f_{\text{max}}}, \]  

were \(2.3 \times 10^{-7}\) s and \(2 \times 10^{-6}\) s respectively. The value \(f\) at the maximum point on the half-circle on the impedance hodograph corresponds to the relaxation frequency and is \(8 \times 10^4\) Hz. The relaxation rate for the pure phase with NASICON structure is usually above \(10^5\) Hz at room temperature [16]. The total ionic conductivity of LAGP at room temperature was \(2.5 \times 10^{-4}\) S/cm.

4. Conclusions

The synthesis of lithium-conducting LAGP solid electrolyte using available water-soluble salts LiNO\(_3\)·3H\(_2\)O, Al(NO\(_3\))\(_3\)·9H\(_2\)O, (NH\(_4\))\(_2\)HPO\(_4\) and citrate \([\text{Ge(C}_6\text{H}_5\text{O}_7)\text{]}^5\) germanium complex was studied.

It is established that the method of preparation of the initial mixture by means of a liquid-phase precursor significantly affects the mechanism of subsequent solid-phase interaction. As a result of the transfer of all initial components to the solution with the formation of a true collective solution, the subsequent interaction proceeded with the formation of a single-phase LAGP product in one stage from an oxalate precursor at 650°C, from a citrate precursor — at 800°C. The total ionic conductivity at room temperature was \(8 \times 10^{-4}\) S/cm and \(2.5 \times 10^{-4}\) S/cm for LAGP synthesized from oxalate and citrate precursor respectively.

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