Reinvestigations of the Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system. Part I: Li\textsubscript{3}AlO\textsubscript{2} and Li\textsubscript{4}AlO\textsubscript{3}

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Reinvestigations of the Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system focused on the synthesis and properties of Li\textsubscript{3}AlO\textsubscript{2} and Li\textsubscript{4}AlO\textsubscript{3} phases have been performed with the help of XRD and IR measuring techniques and Li\textsubscript{2}CO\textsubscript{3}, LiOHH\textsubscript{2}O, Al\textsubscript{2}O\textsubscript{3-sl., α-Al\textsubscript{2}O\textsubscript{3}, Al(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O and boehmite as reactants. Results of investigations have shown the formation of α-, β-, and γ-polytypes of Li\textsubscript{4}AlO\textsubscript{3}. It was found that only the use of LiOHH\textsubscript{2}O as a reactant yields to β-Li\textsubscript{4}AlO\textsubscript{3} as a reaction product. On the other hand, it was proved that Li\textsubscript{3}AlO\textsubscript{2} does not form in the Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system.

A new method for the synthesis of α-Li\textsubscript{3}AlO\textsubscript{2} was developed, consisting in grinding the mixture of Li\textsubscript{2}CO\textsubscript{3} and Al(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O and heating the obtained paste at the temperature range of 400–600°C. The IR spectroscopy was used to characterize obtained phases.

Keywords: Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system, Li\textsubscript{3}AlO\textsubscript{2}, Li\textsubscript{4}AlO\textsubscript{3}, XRD, IR.

INTRODUCTION

Compounds containing lithium have been the subject of comprehensive research for many years due to many different industrial applications, including the production of glass and heat-resistant ceramics\textsuperscript{1–3}, luminescent ionizing radiation detectors\textsuperscript{4–5}, carbon fibre, ceramic, intermetallic, and intermetallic field of lithium-based ceramics have been identified as the most important material for obtaining tritium in Test Modules (TBM) of the International Theronuclear Experimental Reactor Project, ITER\textsuperscript{14–18}.

The literature review has shown that 5 compounds are formed in the two-component system of Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} oxides: Li\textsubscript{3}AlO\textsubscript{2}, Li\textsubscript{4}AlO\textsubscript{3}, Li\textsubscript{2}Al\textsubscript{2}O\textsubscript{4}, Li\textsubscript{4}AlO\textsubscript{3} and Li\textsubscript{3}AlO\textsubscript{4}. Hatch\textsuperscript{19} suggests that limited or continuous solid solutions may form between Li\textsubscript{3}AlO\textsubscript{2} and γ-Al\textsubscript{2}O\textsubscript{3}. So far, no phase diagram of the Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system has been developed in the entire concentration range of the components. There are two versions of the phase diagram of the system in the range of Li\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} in the range of pressures from 0.8 to 0.1 GPa and temperatures from 600 to 1800°C, which shows that one Li\textsubscript{3}AlO\textsubscript{2} compound is formed. In none of these studies, there was any information about the formation of the Li\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} compound, mentioned by M. Kriens\textsuperscript{20, 21} and co-authors\textsuperscript{22}. There are three versions of the phase diagram of the Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system, developed based on thermodynamic data available in the literature\textsuperscript{23–25}.

Despite numerous studies on the Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system, there is still controversy about the number and type of phases formed in it, methods of their preparation and properties\textsuperscript{19–55}. Therefore, our work aimed to verify the literature data on the Li\textsubscript{2}O–Al\textsubscript{2}O\textsubscript{3} system. The first part of our investigations was focused on the Li\textsubscript{3}AlO\textsubscript{2} and Li\textsubscript{4}AlO\textsubscript{3} phases.

The Li\textsubscript{4}AlO\textsubscript{3} compound has four polymorphic modifications:\textsuperscript{26–46} hexagonal α\textsubscript{26–29}, orthorhombic β\textsubscript{30–31}, triclinic γ\textsuperscript{32} and the δ-Li\textsubscript{4}AlO\textsubscript{3} formed at pressures above 9 GPa\textsuperscript{33}. High-pressure studies carried out by Lei et al.\textsuperscript{34} showed that the monoclinic form of β-Li\textsubscript{4}AlO\textsubscript{3} obtained by Cheng\textsuperscript{35} under the pressure of 1.8 GPa is in fact the orthorhombic modification of β-Li\textsubscript{4}AlO\textsubscript{3} and it can be obtained already at the pressure of 0.8 GPa and temperature 623 K. On the other hand, the cubic form of Li\textsubscript{4}AlO\textsubscript{3} described by Debray and Hardy\textsuperscript{36} is in fact the tetragonal γ-Li\textsubscript{4}AlO\textsubscript{3}. Table 1 presents the basic crystallographic data of polymorphic modifications of Li\textsubscript{4}AlO\textsubscript{3}.

The tetragonal γ-Li\textsubscript{4}AlO\textsubscript{3} is considered to be the most thermodynamically stable polymorphic modification of Li\textsubscript{4}AlO\textsubscript{3} and it is considered to be a potential material for obtaining tritium for the purposes of nuclear fusion, substrates for epitaxial growth of II–V semiconductors such as GaN, components for the production of liquid rocket fuel cells or radiation dosimeters\textsuperscript{9, 12, 15–17, 37–39}. In recent years, however, attention has been paid to the hexagonal form of α-Li\textsubscript{4}AlO\textsubscript{3}\textsuperscript{38–44}. It has been shown that at the operating temperature of the fuel cell equal to 650°C, the alpha variety is more stable than the gamma variety\textsuperscript{41}. The α-Li\textsubscript{4}AlO\textsubscript{3} polymorph is also considered as a component for the production of electrode protective layers in lithium batteries\textsuperscript{30–42}. A necessary condition for the use of α-Li\textsubscript{4}AlO\textsubscript{3} however, is to obtain a product containing nanometric grain size.

The literature review shows that the α-Li\textsubscript{4}AlO\textsubscript{3} formed at temperatures not exceeding 600°C is nanocrystalline, however, it is most often contaminated with substrates or by-products of the synthesis reaction\textsuperscript{45, 46}. The large broadening of the diffraction reflections of the α-Li\textsubscript{4}AlO\textsubscript{3} obtained in such conditions is related to the presence of crystallites with dimensions of the order of 7–15 nm and a strong structure defect. SEM and TEM microscopic studies revealed the presence of dislocations and inclusions of spinel-like fragments or amorphous areas in the α-Li\textsubscript{4}AlO\textsubscript{3} samples tested\textsuperscript{46}. On the other hand, at temperatures above 650°C, a slowly progressing phase transition under these conditions begins, leading to the tetragonal γ-Li\textsubscript{4}AlO\textsubscript{3}\textsuperscript{27, 40}.

The conducted literature review showed that the authors of the studies disagreed as to the temperature of phase transitions and the thermal stability of the Li\textsubscript{4}AlO\textsubscript{3} polymorphs. Lejus\textsuperscript{20, 47} found that at 900°C, α-Li\textsubscript{4}AlO\textsubscript{3} undergoes a reversible transformation to the high-temperature γ polymorph however, the transformation from γ to α is very slow. Li\textsubscript{4}AlO\textsubscript{3} melts at 1700°C, but at temperatures higher than 1300°C, it decomposes into Li\textsubscript{2}Al\textsubscript{2}O\textsubscript{5} and Li\textsubscript{2}O caused by the high volatility of lithium oxide. According to Lehmann et al.\textsuperscript{27} slow irreversible
The syntheses of Li₃AlO₃ and LiAlO₂ were carried out using a conventional solid-state reaction method, analogous to that presented in 56–59.

The substrates weighed in suitable proportions were homogenized in an agate mortar and calcined in the temperature range of 400–1200 °C in 24 h stages. The samples were heated in the furnace FCF 3.5/1350 (Czylok, Poland). Temperatures of calcination of samples were estimated basing on literature data concerning Li₂O-Al₂O₃ system 19, 21, 23, 29, 47, 48, 55.

In the frames of this work new method of LiAlO₂ synthesis was developed. Lithium carbonate and aluminium nitrate(V) nonahydrate weighed in stoichiometric proportions were ground in a mortar until the release of CO2 bubbles ceases. The semi-finished product thus obtained was in the form of a paste. Subsequently, the paste obtained was heated in an air atmosphere in the temperature range of 400–600 °C, then, after taking it out of the furnace, it was cooled to room temperature in desiccator, ground in a mortar and subjected to X-ray investigations.

The phase composition of samples was investigated by using XRD method and identified by powder diffraction patterns of obtained samples recorded with the aid of the diffractometer EMPYREAN II (PAnalytical, The Nederlands) using the CuKa radiation with a graphite monochromator with the help of Highscore + software and PDF4+ICDD database. The powder diffraction patterns of selected phases were indexed using the REFINEMENT program of DHN/PDS package.

The IR spectra were recorded on the SPECORD M 80 spectrometer (Carl Zeiss, Jena, Germany). The measurements were made within the wavenumber range of 4000–200 cm⁻¹. The infrared spectra were made by pelleting a sample with KBr in the weight ratio of 1:300.

The mean crystallite size of selected samples was calculated using the Scherrer formula:

\[ D_{hkl} = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \]

where: \( \beta \) – the half-width of the reflex (hkl) [rad], \( D_{hkl} \) – mean crystallite size in the direction perpendicular to the plane (hkl) [Å], \( \lambda \) – wavelength of the X-ray radiation used, \( \lambda = 1.5406 \) [Å], \( k \) – Scherrer’s constant equal to \( k = 0.94 \), \( \theta \) – reflection angle, related to the reflection (hkl) [°].

RESULTS AND DISCUSSION

Transition modifications of alumina such as γ-, η-, δ- and θ- Al₂O₃ obtained in the temperature range

| Formula   | Li₂O [% mol] | Structure type | CS | SG (no.) | Unit cell parameters | Ref |
|-----------|-------------|---------------|----|---------|---------------------|-----|
| α-LiAlO₂  | 50.0        | α-NaFeO₂      | H  | R-3m (166) | 2.7993, 2.793, 14.180 | [29] |
| α-β-LiAlO₂| 50.0        | H             |    |          | 2.8020, 2.8020, 14.2246 | TW  |
| β-LiAlO₂  | 50.0        | β-NaFeO₂      | D Wurzite | Pnma21 (33) | 5.2800, 6.300, 4.900 | [30] |
| γ-LiAlO₂  | 50.0        | γ-LiAlO₂      | T  | P4₁2₁2 (90) | 5.1687, 5.1687, 6.2679 | [33] |
| γ-δ-LiAlO₂| 50.0        | T             |    |          | 5.1724, 5.1724, 6.2756 | TW  |
| δ-LiAlO₂  | 50.0        | D NaCl HP (9 GPa) | T | I4/amd (141) | 3.8866, 3.8866, 8.3001 | [34] |
400–1000 °C have a defective spinel structure based on a cubic close packed lattice of oxide ions\textsuperscript{56, 61}. For this reason, the powder diffraction patterns of individual modifications reported in the literature are similar to each other (similar d\textsubscript{hkl} values). It is very difficult to clearly identify these transition alumina. In this work, when writing about this type of phases, we will use the common symbol Al\textsubscript{2}O\textsubscript{3}-sl (spinel like).

In the first stage of investigations synthesis of Li\textsubscript{2}AlO\textsubscript{3} was carried out using Li\textsubscript{2}CO\textsubscript{3} and α-Al\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}-sl and boehmite as aluminum precursors. Figures 1A and 1B show fragments of powder diffractograms of the reaction mixtures prepared with the use of Al\textsubscript{2}O\textsubscript{3}-sl and Li\textsubscript{2}CO\textsubscript{3} (Fig. 1A) or of α-Al\textsubscript{2}O\textsubscript{3} and Li\textsubscript{2}CO\textsubscript{3} (Fig. 1B) with the compositions corresponding to the Li\textsubscript{2}AlO\textsubscript{3} phase, and samples recorded after successive heating stages in the temperature range of 450–1000 °C.

During the heating stage at 450 °C, almost all boehmite used in the synthesis decomposed to form Al\textsubscript{2}O\textsubscript{3}-sl, and the further synthesis process was carried out in this sample with the use of in situ formed precursor. A single-phase sample containing α-Li\textsubscript{2}AlO\textsubscript{3} was obtained using boehmite and Al\textsubscript{2}O\textsubscript{3}-sl after the heating stage at the temperature of 700 °C. In both cases, the α-Li\textsubscript{2}AlO\textsubscript{3} modification appeared in reaction mixtures after a heating stage at 500 °C. Pure α-Li\textsubscript{2}AlO\textsubscript{3}, obtained after sintering at 700 °C was stable up to the temperature of 900 °C, at which the slow phase change leading to γ-Li\textsubscript{2}AlO\textsubscript{3} began. However, a single-phase sample of γ-Li\textsubscript{2}AlO\textsubscript{3} was obtained only after the heating stage at 1000 °C. The reaction of Li\textsubscript{2}AlO\textsubscript{3} synthesis with the use of corundum was much slower. During it, the α-Li\textsubscript{2}AlO\textsubscript{3} modification appeared in the reaction mixture after a heating stage at 550 °C, but we failed to obtain a single-phase sample of α-Li\textsubscript{2}AlO\textsubscript{3}. On the other hand small amounts of γ-Li\textsubscript{2}AlO\textsubscript{3} were detected after the heating stage at 650 °C while the pure γ-Li\textsubscript{2}AlO\textsubscript{3} was obtained after the heating stage at 950 °C (Fig. 1A and 1B).

In the frames of this work new method of Li\textsubscript{2}AlO\textsubscript{3} synthesis was developed using a mixture of aluminum nitrate(V) and lithium carbonate as reactants. Grinding of the Li\textsubscript{2}CO\textsubscript{3} and Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O solids initiates the reaction between them, as evidenced by CO\textsubscript{2} gas bubbles intensively emitted during the grinding of the reagents in the mortar. The reaction is probably favored by a very large number of crystallization water molecules contained in the crystal lattice of aluminum nitrate(V) nanohydrate, which, released during intense grinding, enables the aluminum nitrate(V) hydrolysis reaction leading to strong acidification of the reaction medium and initiates the decomposition of Li\textsubscript{2}CO\textsubscript{3}. The mechanism of this process is currently being researched and the results will be presented in the next paper. The paste obtained after the evolution of CO\textsubscript{2} bubbles had ceased was then heated in a furnace under an air atmosphere in the temperature range of 400–600 °C. Figure 2 shows the diffractograms recorded after the successive stages of heating the obtained paste.

During the synthesis of α-Li\textsubscript{2}AlO\textsubscript{3} with a new method using Li\textsubscript{2}CO\textsubscript{3} and Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O after the heating steps at the following temperatures: a – 400 °C x 30 min, b – 400 °C x d and c – 600 °C x 30 min. * – means LiNO\textsubscript{3}, ■ – means α-Li\textsubscript{2}AlO\textsubscript{3}

Single-phase sample containing α-Li\textsubscript{2}AlO\textsubscript{3} was obtained after 30 minutes of heating at 600 °C, while the synthesis with Al\textsubscript{2}O\textsubscript{3}-sl and Li\textsubscript{2}CO\textsubscript{3} required heating the reactants at 700 °C. Lithium nitrate(V) melts at 255 °C, and boils and decomposes at 600 °C. The presence of LiNO\textsubscript{3} reflections (PDF 04-010-5519) on the diffractogram of the reaction mixture after the heating step at 400 °C for 30 minutes shows that even molten LiNO\textsubscript{3} slowly reacts with the components of the reaction mixture. The α-Li\textsubscript{2}AlO\textsubscript{3} obtained at the temperature of 600 °C x 30 min was characterized by strongly broadened diffraction reflections, and the average size of crystallites in this preparation determined by the Scherrer method was equal to 75 Å. This value is consistent with the results of the research presented in\textsuperscript{6}, where the effect of calcination time of the α-Li\textsubscript{2}AlO\textsubscript{3} sample at 600 °C on the size of crystallites was analyzed. The reason for the significant broadening of diffraction reflections is, inter alia, a high concentration of defects in the crystal lattice of α-Li\textsubscript{2}AlO\textsubscript{3} obtained at low temperatures\textsuperscript{6}. It should be mentioned, however, that regardless of the type of metal precursors used in the synthesis of α-Li\textsubscript{2}AlO\textsubscript{3}, the reflexes of this phase were considerable broadened. The crystallite size determined by the Scherrer method during the synthesis of α-Li\textsubscript{2}AlO\textsubscript{3} with the use of Li\textsubscript{2}CO\textsubscript{3} and boehmite increased gradually with the increase of temperature from 101 Å (600 °C x 24 h) through 389 Å (700 °C x 24 h) to 406 Å (850 °C x 24 h).

The literature review showed that the Li\textsubscript{2}AlO\textsubscript{3} phase obtained by La Ginestra et al.\textsuperscript{39} is relatively poorly...
studied. Taking into account the comments of the authors of the work, an attempt was made to obtain the Li$_3$AlO$_3$ phase by heating a mixture of LiOH·H$_2$O and Al$_2$O$_3$-sl with a composition corresponding to the Li$_3$AlO$_3$ phase in the temperature range of 400–500 °C. The diffractograms recorded after the first and second heating steps at 400 °C for 72 h resembled that of the Li$_3$AlO$_3$ phase presented by Ginestera. However, X-ray phase analysis showed that the samples obtained at 400 °C were not single-phase and contained a mixture of LiOH (PDF 00-032-0564), Li$_2$CO$_3$ and β-LiAlO$_2$ (PDF 00-033-0785) (Fig. 3).

Figure 3. Fragments of the powder diffraction patterns recorded after successive stages of heating the mixture of LiOH·H$_2$O and Al$_2$O$_3$-sl with the composition corresponding to the formula Li$_3$AlO$_3$: a – 1st stage 400 °C x 72 h, b – 2nd stage 400 °C x 72 h and c – 3rd stage-500 °C x 72 h, where * – LiOH, ● – β-LiAlO$_2$ and ♦ – Li$_2$CO$_3$

However, individual reflections from the Li$_3$AlO$_3$ diffractogram presented by Ginestera were shifted by 0.01–0.20 degrees towards higher 2Theta angles in relation to the position on our diffractograms and data contained in PDF cards of LiOH, Li$_2$CO$_3$ and β-LiAlO$_2$. Therefore, the conducted research shows that the phase with the formula Li$_3$AlO$_3$ is not formed. According to the literature data, LiOH identified in reaction mixtures may be formed as a result of the reaction of Li$_2$O with water contained in the air. LiOH is also formed as a result of dehydration of LiOH·H$_2$O in the temperature range 90–200 °C and then in the temperature range 420–550 °C it decomposes with the release of Li$_2$O. The presence of Li$_2$CO$_3$ in the obtained samples can also be explained because both LiOH·H$_2$O and LiOH have the ability to bind large amounts of CO$_2$ from the air to form Li$_2$CO$_3$. After another heating step at 500 °C for 72 h, the content of β-LiAlO$_2$ in the sample increased significantly. This fact prompted us to try to synthesize β-LiAlO$_2$ using a stoichiometric mixture of LiOH·H$_2$O and Al$_2$O$_3$-sl. Figure 4 shows the diffractograms of the sample with the composition LiAlO$_2$ after subsequent stages of heating. The analysis of the XRD test results showed that the reaction mixture after the first stage of heating at 500 °C for 72 h contained β-LiAlO$_2$ as the main component, accompanied by Li$_2$CO$_3$ and α-LiAlO$_2$ in much smaller amounts. After the second stage of heating at 650 °C for 24 hours, the obtained product contained a mixture of α- and β-LiAlO$_2$, and the intensity of reflections characteristic of α-LiAlO$_2$ increased. The sample after the heating step at 700 °C for 24 h contained γ-LiAlO$_2$ as the main component, accompanied by lower amounts of α- and β-LiAlO$_2$.

Figure 4. Fragments of the powder diffraction patterns recorded after successive stages of heating the mixture of LiOH·H$_2$O and Al$_2$O$_3$-sl with the composition corresponding to the formula LiAlO$_2$: a – 1st stage 500 °C x 72 h, b – 2nd stage 650 °C x 72 h and c – 3rd stage-700 °C x 72 h, where * – α-LiAlO$_2$, ● – β-LiAlO$_2$, ♦ – γ-LiAlO$_2$ and ♦ – Li$_2$CO$_3$

The conducted research indicates that the use of LiOH·H$_2$O as a lithium precursor promotes the formation of β-LiAlO$_2$. However, while striving to eliminate lithium carbonate from the reaction mixture by increasing the reaction temperature, the content of the α-LiAlO$_2$ is simultaneously increased, and above 650 °C β-LiAlO$_2$ undergoes a phase transition to γ-LiAlO$_2$. Currently, research is conducted to obtain a single-phase β-LiAlO$_2$ sample and the results will be published soon.

The powder diffractograms of the β-LiAlO$_2$, γ-LiAlO$_2$ and α-LiAlO$_2$ phases were indexed using the Refinement program. The calculated values of the unit cell parameters are shown in Table 1. In the case of β-LiAlO$_2$, the results of the powder diffractogram pattern indexing are presented in Table 2.

Table 2. The result of the indexing of X-ray powder diffraction pattern of β-LiAlO$_2$ obtained in this work

| Lp. | d$_{exp}$ [nm] | d$_{cal}$ [nm] | (hkl) | I/I$_0$ [%] |
|-----|----------------|----------------|-------|------------|
| 1.   | 4.0479         | 4.0431         | 110   | 10         |
| 2.   | 3.8737         | 3.8693         | 011   | 86         |
| 3.   | 3.1218         | 3.1194         | 111   | 16         |
| 4.   | 2.7050         | 2.7039         | 120   | 100        |
| 5.   | 2.6377         | 2.6362         | 200   | 55         |
| 6.   | 2.4532         | 2.4516         | 002   | 59         |
| 7.   | 2.3690         | 2.3679         | 121   | 25         |
| 8.   | 2.3237         | 2.3219         | 201   | 10         |
| 9.   | 2.1787         | 2.1766         | 211   | 4          |
| 10.  | 2.0987         | 2.0963         | 112   | 6          |
| 11.  | 1.9299         | 1.9302         | 031   | 3          |
| 12.  | 1.8149         | 1.8126         | 131   | 22         |
| 13.  | 1.7958         | 1.7953         | 202   | 9          |
| 14.  | 1.7270         | 1.7265         | 212   | 2          |
| 15.  | 1.6419         | 1.6424         | 230   | 1          |
| 16.  | 1.5997         | 1.6001         | 311   | 4          |
| 17.  | 1.5745         | 1.5748         | 040   | 5          |
| 18.  | 1.5343         | 1.5347         | 320   | 34         |
| 19.  | 1.3980         | 1.3987         | 123   | 16         |
| 20.  | 1.3892         | 1.3891         | 203   | 6          |
To know better properties of obtained phases IR spectra of γ-LiAlO2, β-LiAlO2 and α-LiAlO2 were recorded. Analysis of the number and positions of absorption bands recorded in their IR spectra has shown good agreement with literature data32, 47, 50–52.

The results of XRD and IR investigations showed that β-LiAlO2 crystallizes in an orthorhombic system.

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