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# Effect of Water Vapor Pressure on the Phase Composition of Lithium Monoaluminates Formed in the Interaction of Aluminum Hydroxide and Lithium Carbonate

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**Abstract**—It is shown that the partial water vapor pressure affects the phase composition of lithium monoaluminates formed when aluminum hydroxide (gibbsite) and lithium carbonate are heated in air, in the atmosphere of helium, and in a dynamic vacuum. When the mixture is heated to 800°C in an air atmosphere with partial water pressure of 1300 Pa, a nearly single-phase lithium monoaluminate $\alpha$-$LiAlO_2$ is formed. In the reaction in the atmosphere of helium, in which the partial water vapor pressure does not exceed 4 Pa, $\gamma$-$LiAlO_2$ is formed together with $\alpha$-$LiAlO_2$, with the content of the former exceeding that produced in the reaction in air. When the mixture is heated under dynamic vacuum conditions with partial water vapor pressure lower than 0.1 Pa, mostly $\gamma$-$LiAlO_2$ is formed.

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Highly dispersed lithium aluminates ($\alpha$-$LiAlO_2$, $\gamma$-$LiAlO_2$) find use as materials for the matrix electrolyte of melted-carbonate fuel cells [1, 2]. One of promising ways to synthesize these substances is based on a thermal treatment of a mixture of aluminum hydroxide (gibbsite) and lithium carbonate in air at temperatures exceeding 600°C [3–6]. It has been shown that nearly single-phase $\alpha$-$LiAlO_2$ is formed in the temperature range 600–700°C. At higher temperatures, $\gamma$-$LiAlO_2$ is formed together with $\alpha$-$LiAlO_2$, with the content of the former increasing as the thermal treatment temperature is raised. $\alpha$-$LiAlO_2$ is formed in a thermal treatment in air, i.e., at rather high partial water vapor pressures, via the interaction of lithium carbonate and crystalline aluminum oxides $\gamma$-$Al_2O_3$ and $\chi$-$Al_2O_3$ formed in the decomposition of gibbsite contained in the mixture [4–6]. At low water vapor pressures (below 1–4 Pa), the decomposition of gibbsite yields X-ray-amorphous $\rho$-$Al_2O_3$ [7], whose structure is strongly different from that of crystalline aluminum oxides [8, 9]. Therefore, it can be assumed that the phase composition of lithium monoaluminates being formed may depend on the water vapor pressure at which the process is performed.

The goal of our study was to find a way to control the phase composition of lithium monoaluminates obtained in thermal treatment of a mixture of crystalline aluminum hydroxide (gibbsite) and lithium carbonate by varying the partial water vapor pressure when performing the chemical reaction.

## EXPERIMENTAL

We used crystalline aluminum trihydroxide (gibbsite) of analytically pure grade and chemically pure lithium carbonate. Experiments were performed with a mixture of the starting components and a mixture subjected to a preliminary mechanical treatment in an AGO-2 planetary activator. The mechanical treatment was performed in air in the AGO-2 planetary centrifugal mill in 100-mL steel drums at acceleration of 40 g for 1 min. The activation was performed with steel balls 5 mm in diameter. The mass ratio of the substance to that of the ball load was 1 : 20. High-temperature in situ measurements were made on a Bruker D8 Advance diffractometer (Germany) with Cu$K_{\alpha}$ radiation in the 2θ range 12–70° at a step of 0.02° and accumulation time of 35 s. A sample was heated in an Anton Paar HTK 1200N chamber (Austria) in a corundum cuvette in air, flow of helium, or dynamic vacuum (~5 × $10^{-4}$ Torr) in steps at a heating rate of 12 deg $min^{-1}$. After temperatures of 100, 200, 300, 400, 500, 600, 700, and 800°C were reached, the heating was interrupted and X-ray diffraction (XRD) patterns were recorded. The vacuum was created with an Edwards RV3 roughing pump and Edwards EXT76DX turbo-molecular pump (Great Britain). Helium containing less than 0.004% of water was used; the helium flow rate was 70 mL $min^{-1}$. The phase composition of the synthesis products was

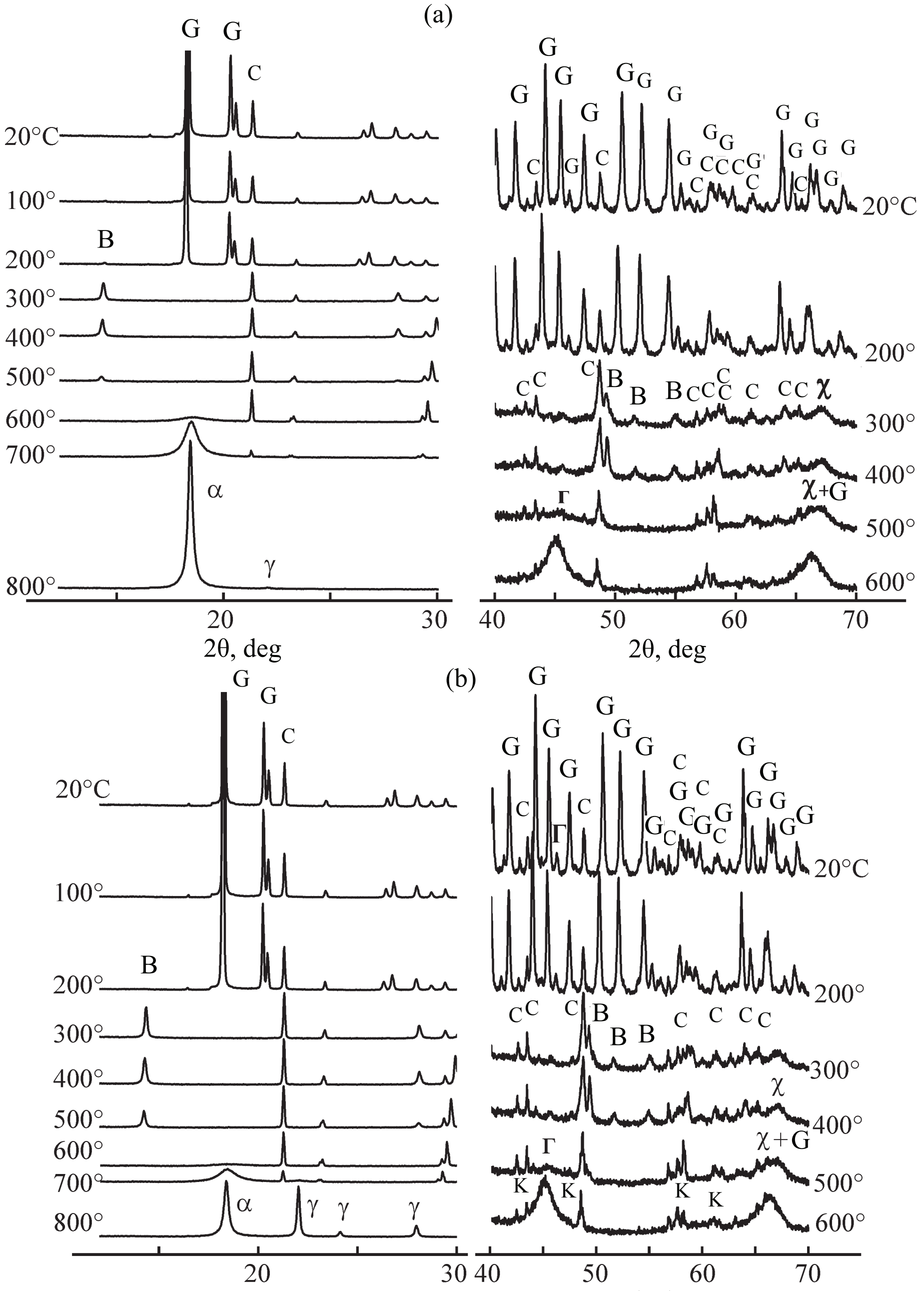

**Fig. 1.** In situ diffraction patterns of the starting mixture of aluminum hydroxide and lithium carbonate in (a) air, (b) atmosphere of helium, and (c) dynamic vacuum. (G) $Al(OH)_3$, (C) $Li_2CO_3$, (B) AlO(OH), (χ) χ-$Al_2O_3$, (g) γ-$Al_2O_3$, (α) α-$LiAlO_2$, (γ) γ-$LiAlO_2$. (2θ) Bragg angle; the same for Fig. 2.

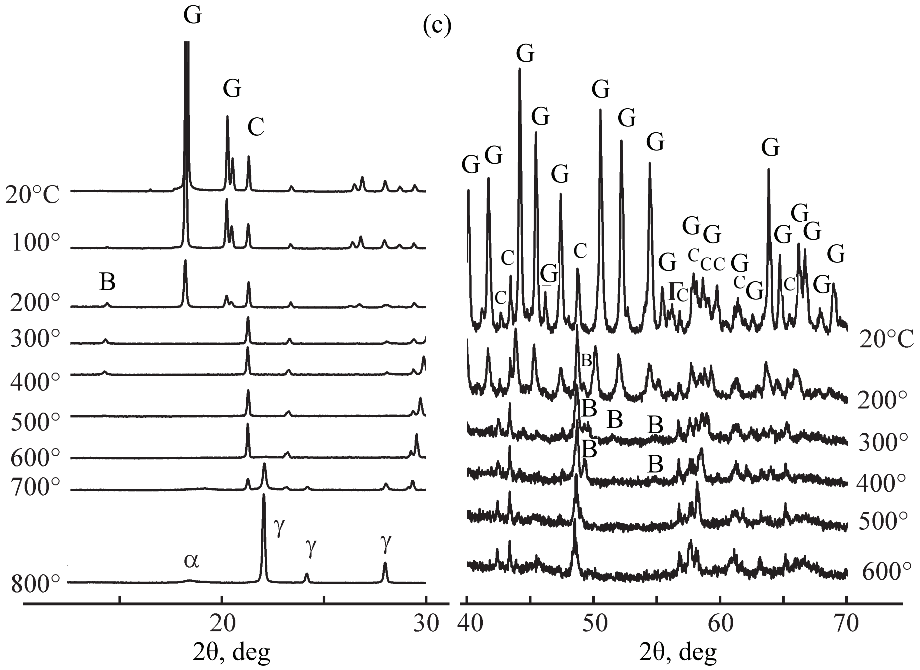

**Fig. 1.** (Contd.).

analyzed with the use of PDF-4 powder database (2011). A quantitative analysis of phases was made by simulating an XRD pattern by the Rietveld method with Topas 4.2 software (Bruker AXS, Germany).

## RESULTS AND DISCUSSION

**Study of processes occurring in the interaction of a mixture of crystalline aluminum hydroxide and lithium carbonate in air, atmosphere of helium, and vacuum.** XRD data indicate that the phase composition of the mixture hardly changes when the mixture of $Al(OH)_3$ and $Li_2CO_3$ is heated from room temperature to 200°C (Fig. 1a). In the temperature range 200–300°C, $Al(OH)_3$ decomposes to give boehmite, the content of which remains nearly unchanged in the temperature range 300–400°C. Boehmite starts to decompose at 400–500°C, with this process being nearly complete as 600°C is reached. The formation of a broadened peak at $2\theta = 67°$ at 300–400°C indicates that $\chi$-$Al_2O_3$ appears due to the decomposition of gibbsite. At 500°C, a broadened peak appears at $2\theta = 45°$ in addition to the increase in the integral intensity of the peak at $2\theta = 45°$, which indicates that $\gamma$-$Al_2O_3$ is formed due to the decomposition of boehmite. The content of lithium carbonate remains nearly unchanged upon heating to 500°C; above this temperature, the intensity of $Li_2CO_3$ reflections falls, which shows that lithium carbonate interacts with aluminum oxides. This interaction is evidenced by the appearance at 600°C of weak broadened reflections characteristic of $\alpha$-$LiAlO_2$, with their intensity growing as the temperature is raised further. Analysis of the XRD pattern of a sample, obtained at 800°C, by the Rietveld method shows that weak $\gamma$-$LiAlO_2$ reflections are observed together with $\alpha$-$LiAlO_2$, which is the main phase (see the table).

Heating in the atmosphere of helium to 600°C affects only slightly the composition and content of intermediate phases, compared with the decomposition in air (Fig. 1b). The most pronounced differences in the phase composition are observed on heating the mixture to 700°C and more. In this case, the appearance of higher intensity reflections of the gamma form is observed together with alpha-lithium aluminate.

When a mixture of aluminum hydroxide and lithium carbonate is heated in a vacuum, a somewhat different pattern of phase transformations is observed (Fig. 1c). Aluminum hydroxide decomposes in the temperature range 100–200°C, the amount of boehmite formed in this case is substantially smaller as compared with the decomposition in air. As also in the case of heating in air, heating to 500°C leads to a nearly complete disappearance of boehmite-related reflections. The substantially lower intensity of the reflections at $2\theta = 45$ and 67° points to a very low content of $\gamma$-$Al_2O_3$ and $\chi$-$Al_2O_3$ in the products formed when aluminum hydroxide decomposes in a vacuum. When the mixture is thermally treated in a vacuum, the intensity of lithium carbonate reflections remains nearly unchanged up to 600°C, as it also does in the case of treatment in air. Weak reflections associated with $\alpha$-$LiAlO_2$ and $\gamma$-$LiAlO_2$ appear at this temperature. Further increase in temperature to 800°C results in that mostly $\gamma$-$LiAlO_2$ is formed with a certain admixture of $\alpha$-$LiAlO_2$ (see the table and Figs. 1 and 2).

**Analysis of interaction processes occurring when a mechanically activated mixture of crystalline**

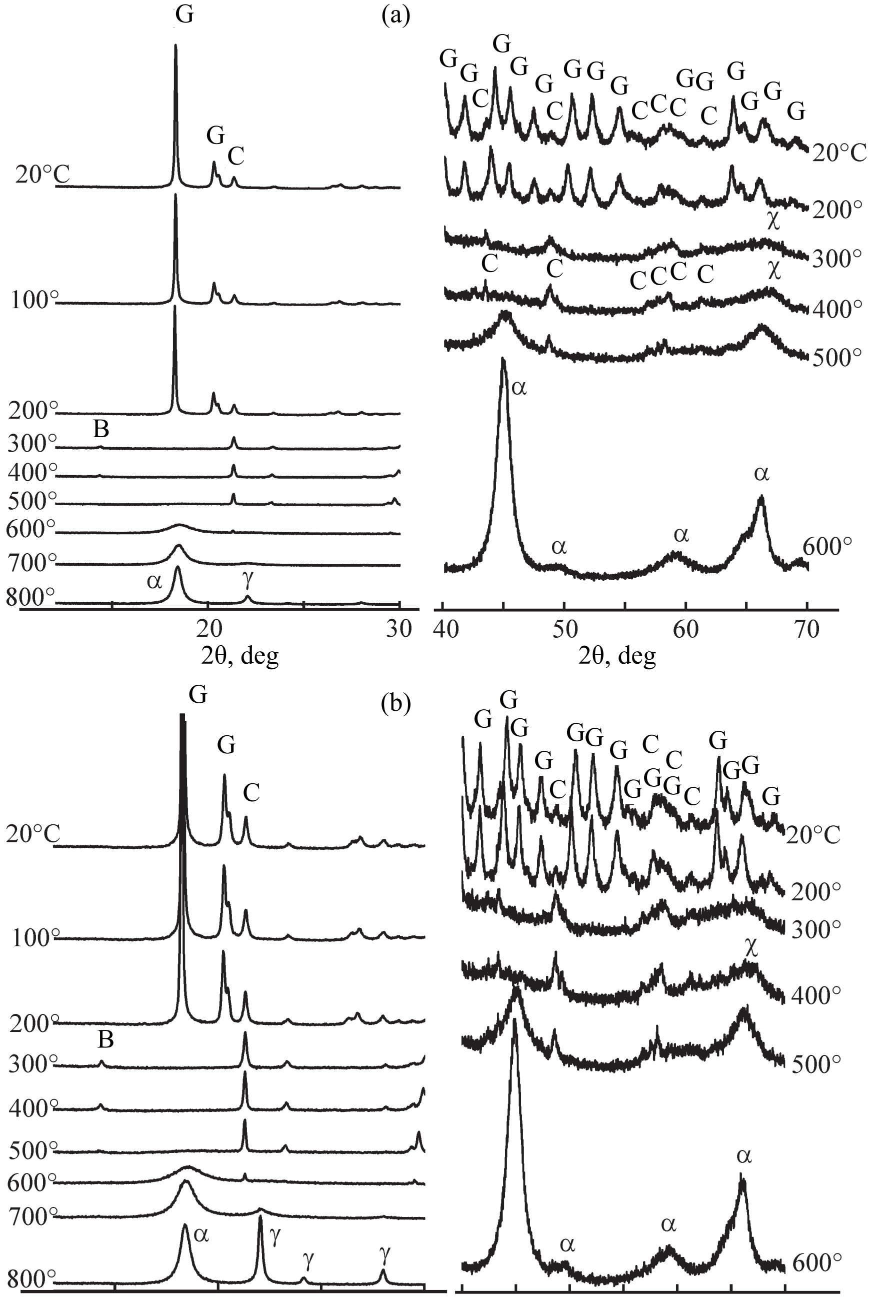

**Fig. 2.** In situ X-ray diffraction patterns of mechanically activated mixture of aluminum hydroxide and lithium carbonate in (a) air, (b) atmosphere of helium, and (c) dynamic vacuum. (G) $Al(OH)_3$, (C) $Li_2CO_3$, (B) AlO(OH), ($\chi$) $\chi$-$Al_2O_3$, (g) $\gamma$-$Al_2O_3$, ($\alpha$) $\alpha$-$LiAlO_2$, ($\gamma$) $\gamma$-$LiAlO_2$.

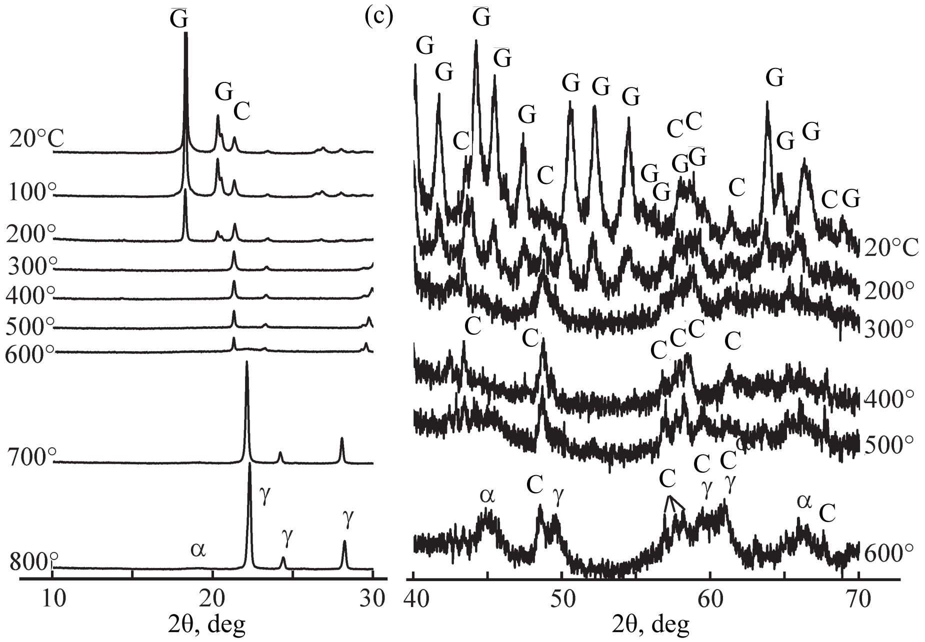

**Fig. 2.** (Contd.).

**aluminum hydroxide and lithium carbonate is heated in air, in the atmosphere of helium, and in a vacuum.** The processes occurring when nonactivated and activated mixtures are thermally treated in air are qualitatively similar. The only difference is that a lower content of boehmite is observed in thermal treatment of an activated mixture (Fig. 2a). The decrease in the amount of boehmite results in that the main aluminum oxide formed in decomposition of aluminum trihydroxide is $\chi$-$Al_2O_3$, whose formation is evidenced by the appearance of a broadened reflection at $2\theta = 67°$. Mostly $\alpha$-$LiAlO_2$ is formed at 700°C, with an admixture of $\gamma$-$LiAlO_2$, the content of which grows as the temperature is raised to 800°C.

Heating in the atmosphere of helium to 800°C leads to an increase in the content of $\gamma$-$LiAlO_2$, compared with the heating in air (Fig. 2b).

Compared with the heating in air, the decomposition in a vacuum leads to significant change in the XRD patterns (Fig. 2c). A decrease in the decomposition temperature of aluminum hydroxide is observed: it decomposes in the temperature range 100–200°C. In the case of decomposition in a vacuum, formation of the boehmite phase and reflections of the aluminum oxides $\gamma$-$Al_2O_3$ and $\chi$-$Al_2O_3$ are hardly observed. At 600°C, weak reflections of $\alpha$-$LiAlO_2$ and $\gamma$-$LiAlO_2$ are observed, with the intensity of the latter growing as the treatment temperature is raised. In contrast to the decomposition in air, the final product synthesized at 800°C mostly contains $\gamma$-$LiAlO_2$ (see the table, Fig. 2a).

The data we obtained indicate that the phase composition of lithium monoaluminates formed when a mixture of aluminum hydroxide (gibbsite) and lithium carbonate is heated within the stability range of $\alpha$-$LiAlO_2$

Content of the lithium monoaluminates $\alpha$-$LiAlO_2$ and $\gamma$-$LiAlO_2$ in the products formed in the thermal treatment with heating to 800°C of the starting and mechanically activated mixtures in air, atmosphere of helium, and dynamic vacuum

| Activation duration, min | Concentration, wt % | | | | | |
|---|---|---|---|---|---|---|
| | air | | helium | | vacuum | |
| | $\gamma$-$LiAlO_2$ | $\alpha$-$LiAlO_2$ | $\gamma$-$LiAlO_2$ | $\alpha$-$LiAlO_2$ | $\gamma$-$LiAlO_2$ | $\alpha$-$LiAlO_2$ |
| 1 | 22 | 78 | 43 | 57 | 92 | 8 |
| 0 | 1 | 99 | 46 | 54 | 88 | 12 |

(600–700°C) and at higher temperatures (800°C) depends on the partial water vapor pressure at which the reaction is performed. When the process is carried out in the air atmosphere for which the partial water vapor pressure is about 1300 Pa, mostly $\alpha$-$LiAlO_2$ is formed in the temperature range under study, with a minor admixture of $\gamma$-$LiAlO_2$. When the mixture is heated in the atmosphere of helium, in which the partial water vapor pressure does not exceed 4 Pa, $\gamma$-$LiAlO_2$ is formed together with $\alpha$-$LiAlO_2$, with the content of the former exceeding that produced in the case of decomposition in air. Under the dynamic vacuum conditions in which the partial water vapor pressure is lower than 0.1 Pa, mostly $\gamma$-$LiAlO_2$ is formed. A qualitatively similar effect of the water vapor pressure is also observed for a mixture subjected to a 1-min mechanical treatment, in which the reagents are mostly dispersed and mixed [6]. In our opinion, a possible reason for this dependence of the phase composition of lithium monoaluminates on the partial water vapor pressure is that gibbsite decomposes upon a thermal treatment of the reagent mixture at a high partial water vapor pressure to give crystalline aluminum oxides. These oxides interact with lithium carbonate to give mostly $\alpha$-$LiAlO_2$. In the reaction in a dynamic vacuum at low partial water vapor pressures, the decomposition of gibbsite is accompanied by the formation of the X-ray-amorphous aluminum oxide whose interaction with lithium carbonate yields $\gamma$-$LiAlO_2$ at 600–700°C, i.e., in the stability range of $\alpha$-$LiAlO_2$. The assumption that $\gamma$-$LiAlO_2$ can be formed due to the interaction of the X-ray-amorphous aluminum oxide with lithium carbonate is supported by the data of [10], where it was shown that, when a mixture of lithium carbonate and preliminarily synthesized X-ray-amorphous aluminum oxide is heated in air at 600–700°C, $\gamma$-$LiAlO_2$ is formed. The thermal treatment in a flow of helium gives, despite the rather low content of water vapor, not only X-ray-amorphous aluminum oxide, but also crystalline oxides. This is probably due to the increase in the partial water vapor pressure over the surface of the solid phase in the decomposition of gibbsite. The data we obtained demonstrate that the phase composition of lithium monoaluminates can be controlled by varying the partial water vapor pressure when the chemical reaction is performed.

## CONCLUSIONS

It was demonstrated that the partial water vapor pressure at which the process is performed strongly affects the phase composition of lithium monoaluminates formed when a mixture of lithium carbonate and aluminum hydroxide is heated. Varying the partial water vapor pressure makes it possible to obtain in the same thermal treatment modes various modifications of highly dispersed lithium monoaluminates ($\alpha$-$LiAlO_2$, $\gamma$-$LiAlO_2$), which is of interest for development of methods for synthesis of these compounds.

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