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# Mechanically Stimulated Thermal Synthesis of Lithium Pentaaluminate from Lithium Carbonate and Aluminum Hydroxide

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**Abstract**—It is shown that the phase composition of lithium aluminates formed when aluminum hydroxide in the form of gibbsite interacts with lithium carbonate in their mixture with Al : Li atomic ratio of 5 : 1 depends on the duration of a preliminary mechanical activation of the mixture and on the temperature of the subsequent thermal treatment. A thermal treatment of the starting mixture at temperatures exceeding 800°C yields $LiAl_5O_8$ with a substantial admixture of α- and γ-$LiAlO_2$. Raising the duration of the mechanical activation to 5 min and more makes it possible to obtain highly dispersed single-phase $LiAl_5O_8$ with a specific surface area larger than 20 $m^2$ $g^{-1}$

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Highly dispersed lithium pentaaluminate $LiAl_5O_8$ is used in catalysis as a catalyst support [1, 2] and as a matrix for synthesis of phosphors [3–5]. The ceramic method for synthesis of this compound, based on the calcination of a mixture of lithium carbonate and aluminum oxide, requires a high temperature (1100°C) and long reaction duration (12 h) [6]. Another approach to synthesis of this compound is based on the sol-gel method [7], which includes mixing and hydrolysis with water of a mixture of aluminum isopropylate and lithium nitrate, followed by drying of the gel and its thermal treatment in air at 800°C. To a shortcoming of this method can be attributed the use of expensive starting reagents and the formation as a result of synthesis of by-products, which should be utilized. One of promising ways to synthesize complex oxides, which has been actively developed during the last 10–15 years, is the mechanochemical method [8, 9]. As applied to lithium aluminates, this method has been implemented in synthesis of γ-$LiAlO_2$. A highly dispersed γ-$LiAlO_2$ with specific surface area larger than 10 $m^2$ $g^{-1}$ was obtained with a preliminary mechanical treatment of a mixture of aluminum hydroxide (gibbsite) and lithium carbonate in an AGO-2 planetary activator at a centrifugal acceleration of 40 g, with the subsequent thermal treatment of activation products in air at temperatures exceeding 700°C [10]. This method attracts attention because of the simple implementation, ecological safety, and possibility of using readily available and comparatively inexpensive salts of lithium carbonate and aluminum hydroxide compounds.

The goal of our study was to examine the possibility of performing a mechanochemical synthesis of lithium pentaaluminate with mechanical activation of a mixture of aluminum hydroxide (gibbsite) and lithium carbonate and the subsequent thermal treatment of the activation products in air.

## EXPERIMENTAL

The starting mixture was prepared from the following reagents: crystalline aluminum hydroxide $Al(OH)_3$ (gibbsite) of analytically pure grade [GOST (State Standard) 11841–76] with specific surface area of 0.2 $m^2$ $g^{-1}$ and lithium carbonate $Li_2CO_3$ of chemically pure grade [TU (Technical Specification) 6-09-3728–83] with specific surface area of 0.7 $m^2$ $g^{-1}$. The starting reagents were mixed in a $Li_2CO_3$ : $Al(OH)_3$ molar ratio of 1 : 10, necessary for obtaining $LiAl_5O_8$, and then

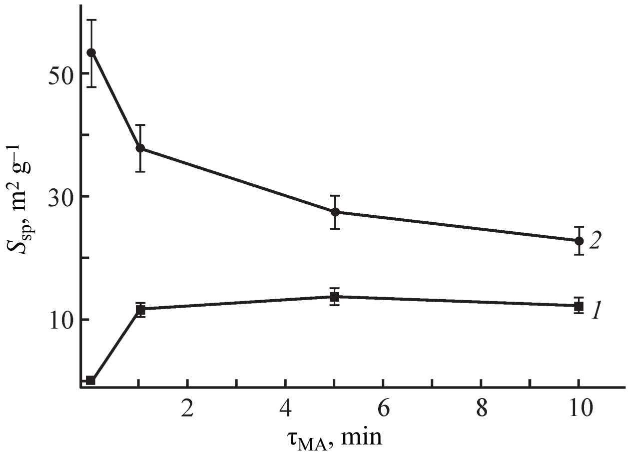

**Fig. 1.** Dependence of the specific surface area $S_{sp}$ of (*1*) mixtures of aluminum hydroxide and lithium carbonate and (*2*) products of their thermal treatment on the duration $\tau_{MA}$ of mechanical activation. Thermal treatment conditions: 900°C, 2 h, air.

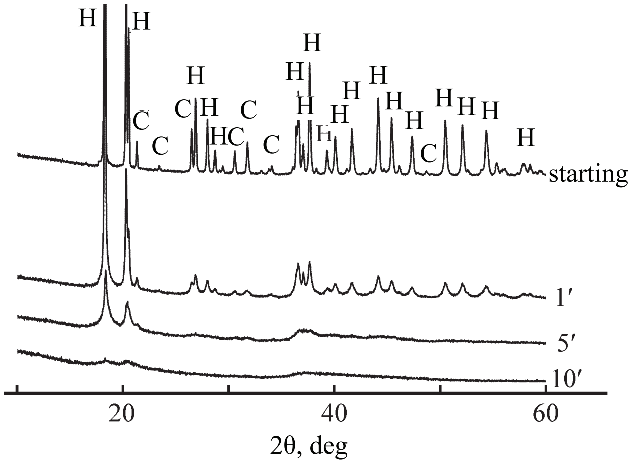

**Fig. 2.** XRD data for products of the mechanical activation of a mixture of aluminum hydroxide and lithium carbonate at process durations of 1, 5, and 10 min. (2θ) Bragg angle; the same for Figs. 5–9. (H) $Al(OH)_3$ and (C) $Li_2CO_3$.

were activated in an AGO-2 planetary centrifugal mill at acceleration of 40 g for 1, 5, and 10 min. For the treatment durations of 5 and 10 min, the activation was performed discretely, during 2.5 min with a break in between. The activation was performed in air in 100-mL steel drums with steel balls 5 mm in diameter. The ratio between the substance mass and the mass of the ball load (200 g) was 1 : 20.

The samples obtained after the mechanical activation of the mixture of the starting reagents and their heating in air were examined by X-ray diffraction (XRD) analysis, in situ XRD analysis, thermal analysis, and measurement of the specific surface area and particle size. The XRD patterns were recorded with a D8 Advance diffractometer with CuKα radiation, measurement range 2θ = 10–70° with a step of 0.02° and accumulation duration of 35 s. High-temperature in situ XRD measurements were made in an Anton Par HTK 1200N chamber (Austria) with a corundum cuvette. The heating was performed in air in stages from room temperature to 100°C at a rate of 12 deg min$^{-1}$. Then, an XRD pattern was recorded at this temperature at angles in the range 2θ = 10–60°. After the recording was complete, the sample was heated to 200°C and an XRD pattern was recorded, etc. The thermal treatment of a mechanically activated mixture was performed in air in a SNOL muffle furnace at a heating rate of 10 deg min$^{-1}$. After 900°C was reached, the mixture was kept at this temperature for 2 h. A quantitative analysis of phases was made by modeling the profile of the XRD pattern by the Rietveld method with Topas 4.2 software (Bruker AXS, Germany). A thermogravimetric analysis was made in air on a modified MOM derivatograph (Hungary) in the temperature range 20–800°C in corundum crucibles at a heating rate of 10 deg min$^{-1}$. The specific surface area was estimated by the chromatographic method on the basis of argon desorption with the use of a standard sample. The dispersity was measured with a Microsizer-201A laser particle dispersity meter, with ethanol serving as the dispersion medium.

## RESULTS AND DISCUSSION

**Mechanical activation of a mixture of $Al(OH)_3$ and $Li_2CO_3$.** The dependence of the specific surface area of the mixture on its activation duration is nonmonotonic (Fig. 1). The specific surface area increases when the activation duration is up to 5 min. Further, it decreases with increasing time of mechanical activation. The significant (by two orders of magnitude) increase in the specific surface area is indicative of a strong dispersion of reagents to give submicrometer particles of aluminum hydroxide and lithium carbonate. The mechanical activation leads not only to the dispersion of reagents, but also changes their microstructure and structure. For example, even after 1-min activation, the integral intensity of the reflections of aluminum hydroxide and lithium carbonate strongly decreases and their width

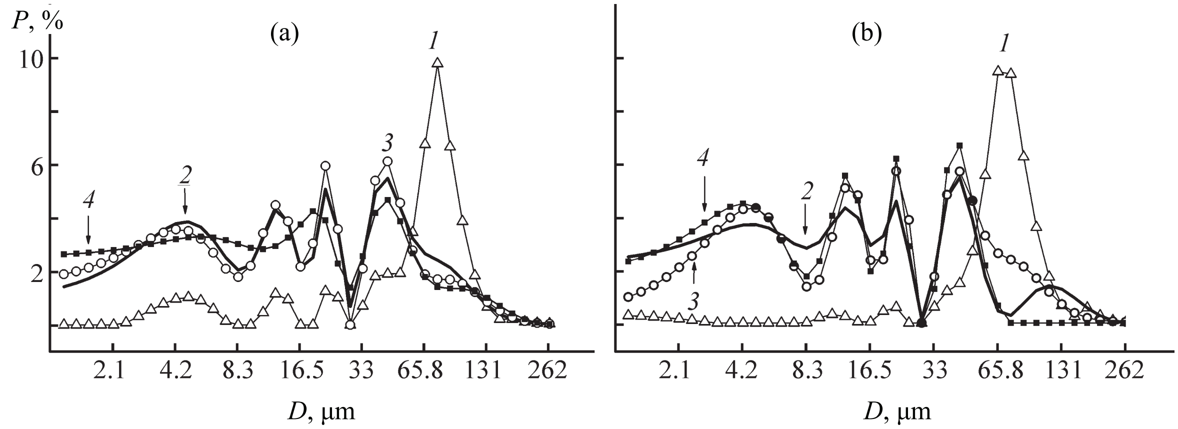

**Fig. 3.** Particle size (*D*) distribution *P* for (a) mixture of aluminum hydroxide and lithium carbonate and (b) products of a thermal treatment of a mechanically activated mixture. Duration of mechanical activation (min): (*1*) 0, (*2*) 1, (*3*) 5, (*4*) 10; the same for Fig. 9.

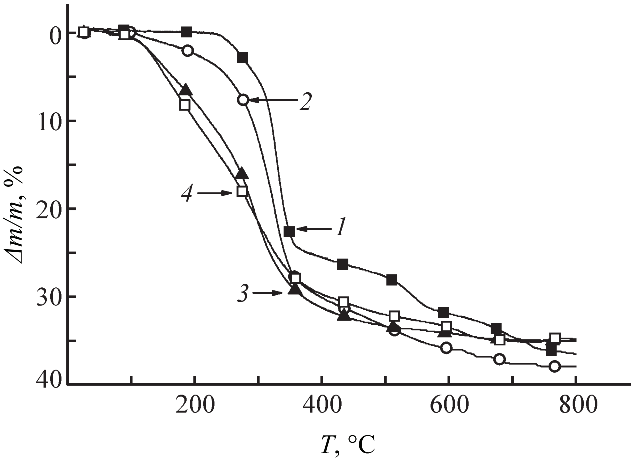

**Fig. 4.** Thermograms of (*1*) starting mixture of aluminum hydroxide and lithium carbonate and products of its mechanical activation for (*2*) 1, (*3*) 5, and (*4*) 10 min. Heating rate 10 deg min$^{-1}$, air as atmosphere. ($\Delta m/m$) Loss of mass and (*T*) temperature.

grows (Fig. 2). Raising the activation duration to 5 min leads to a further decrease in the integral intensity and broadening of the reflections of these compounds. Finally, 10-min activation is accompanied by the formation of a nearly X-ray-amorphous product.

Most part of the starting mixture contains aggregates 30 to 150 μm in size, which predominantly belong to aluminum hydroxide (Fig. 3a). Activation of the mixture for 1 min leads to a decrease in the share of the coarse fraction and makes higher the share of fine fractions with sizes less than 30 μm. Raising the mechanical treatment duration to 5 min affects only slightly the particle size distribution. Activation for 10 min results in that the particle size distribution changes in the <30 μm range.

**Study of processes occurring in thermal treatment of the starting and mechanically activated mixture of aluminum hydroxide and lithium carbonate.** Three stages in the change in the mass of the substance can be distinguished in the thermogram of the unactivated mixture. The first stage begins at temperatures higher than 220°C and ends at 320–350°C (Fig. 4). As indicated by in situ XRD data, this stage is associated with the dehydration of aluminum hydroxide to give boehmite and χ-aluminum oxide (Fig. 5). The second stage begins at a temperature higher than 450°C and ends at 550–570°C. It is mostly associated with the decomposition of boehmite to give gamma aluminum oxide (Fig. 4). The third stage, observed at temperatures higher than 570°C, is associated with the interaction of lithium carbonate with aluminum oxides. This is evidenced by the decrease in the integral intensity of lithium carbonate reflections and by the appearance at 600°C of broadened reflections characteristic of α-$LiAlO_2$. $LiAl_5O_8$ reflections start to appear, together with the α-$LiAlO_2$ reflections, at 700°C, and their intensity grows with increasing temperature.

A preliminary mechanical activation of the mixture for 1 min results in that the onset temperature of the thermal decomposition of aluminum hydroxide decreases by more than 100°, the loss of mass in the stage of aluminum hydroxide dehydration (100–350°C) increases, and the loss of mass in the stage of boehmite dehydration (450–570°C) decreases (Fig. 4). The amount of boehmite formed in the stage of aluminum hydroxide dehydration is substantially smaller, compared with the unactivated mixture (Fig. 6). The lithium carbonate reflections start to decrease in intensity in the temperature range 400–500°C. At 500°C, there appear broadened reflections peaked

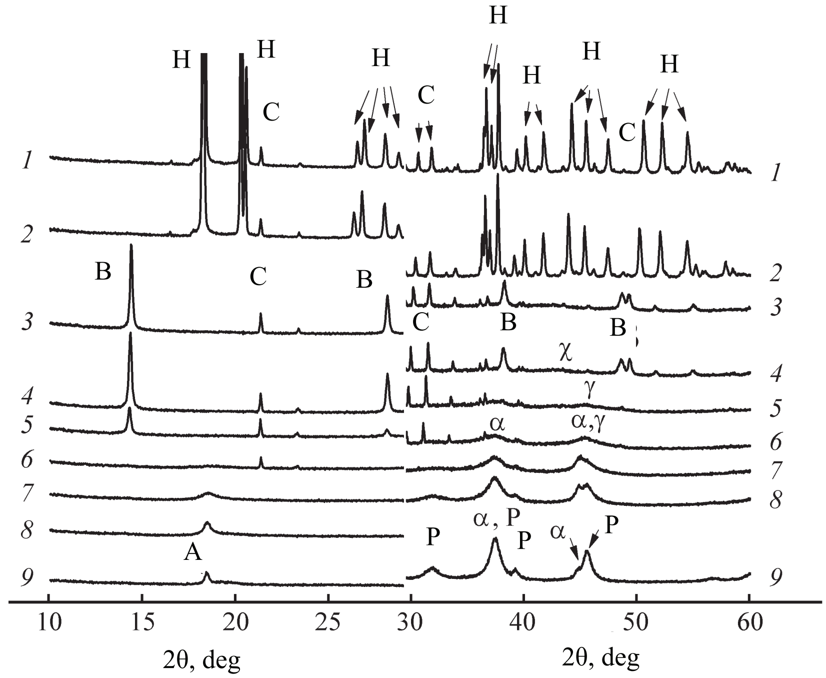

**Fig. 5.** In situ X-ray diffraction patterns of the starting mixture of aluminum hydroxide and lithium carbonate in air. *T* (°C): (*1*) 30, (*2*) 200, (*3*) 300, (*4*) 400, (*5*) 500, (*6*) 600, (*7*) 700, (*8*) 800, (*9*) 900; the same for Figs. 6 and 8. Reflections: (H) $Al(OH)_3$; (C) $Li_2CO_3$; (B) AlO(OH); (α) α-$LiAlO_2$; (P) $LiAl_5O_8$; (χ) χ-$Al_2O_3$; (γ) γ-$Al_2O_3$.

at 2θ = 37.4 and 45°, which can be attributed both to χ-$Al_2O_3$ (37.4°) and to $LiAl_5O_8$ (37.4, 45.4°). Raising the temperature leads to an increase in the intensity and decrease in the width of the $LiAl_5O_8$ reflections. At 800°C and more, weak reflections of γ-$LiAlO_2$ are recorded together with those of lithium pentaaluminate.

Raising the activation duration of the mixture to 5 min intensifies the dehydration of the hydroxide (Fig. 4). The change in mass (30%), observed in the temperature range 100–350°C, corresponds to the nearly full dehydration of aluminum hydroxide (31.6%) in the mixture. The dehydration of aluminum hydroxide does

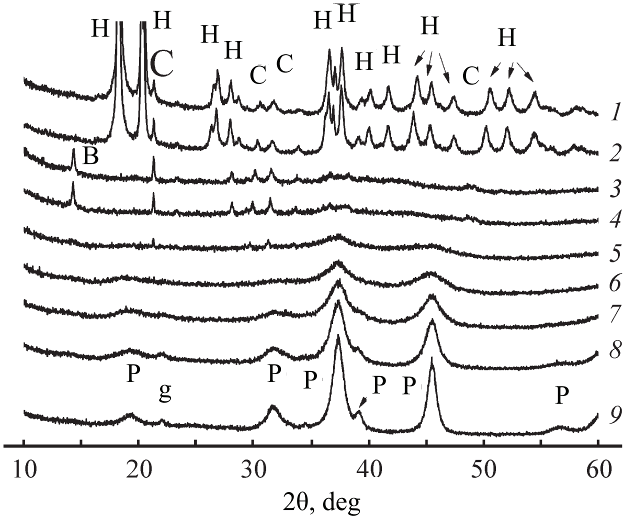

**Fig. 6.** In situ X-ray diffraction patterns of a mixture of aluminum hydroxide and lithium carbonate, mechanically activated for 1 min, in air. Reflections: (H) $Al(OH)_3$; (C) $Li_2CO_3$; (B) AlO(OH); (α) α-$LiAlO_2$; (P) $LiAl_5O_8$.

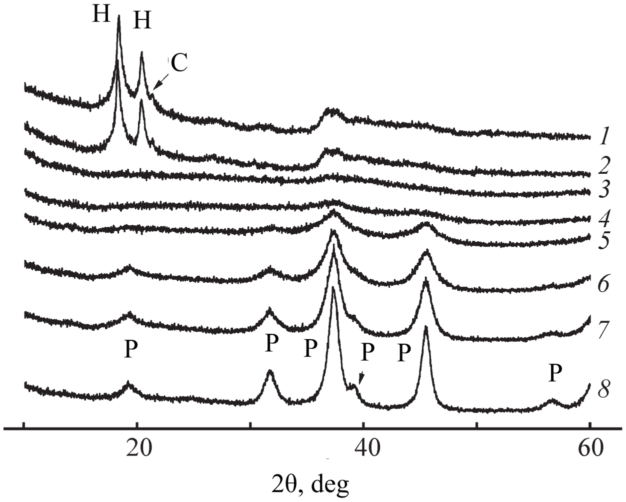

**Fig. 7.** In situ X-ray diffraction patterns of a mixture of aluminum hydroxide and lithium carbonate, mechanically activated for 5 min, in air. *T* (°C): (*1*) 30, (*2*) 200, (*3*) 300, (*4*) 500, (*5*) 600, (*6*) 700, (*7*) 800, (*8*) 900. Reflections: (H) $Al(OH)_3$; (C) $Li_2CO_3$; (P) $LiAl_5O_8$.

Phase composition of products formed after the thermal treatment of mechanically activated mixtures of lithium carbonate and aluminum hydroxide. Temperature of the thermal treatment, 900°C; treatment duration 2 h

| MA duration, min | Weight percent | | |
|---|---|---|---|
| | $\alpha$-$LiAlO_2$ | $\gamma$-$LiAlO_2$ | $LiAl_5O_8$ |
| 0 | 8.3 | 2.8 | 88.9 |
| 1 | 0.3 | 1.5 | 98.2 |
| 5 | – | – | 100 |
| 10 | – | – | 100 |

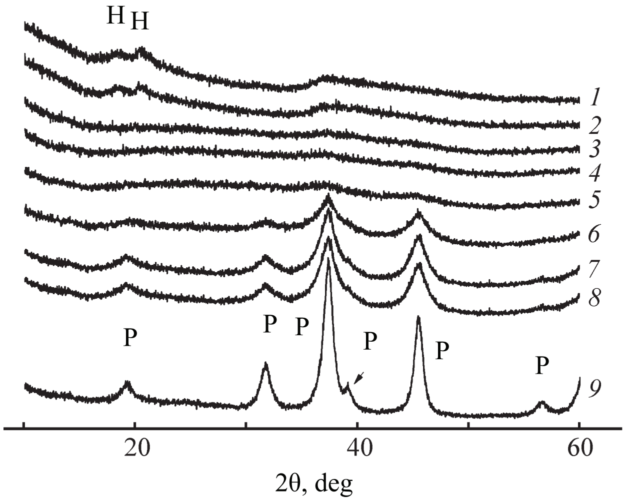

**Fig. 8.** XRD in situ analysis of a mixture of aluminum hydroxide and lithium carbonate, mechanically activated for 10 min, in air. Reflections: (H) $Al(OH)_3$; (P) $LiAl_5O_8$.

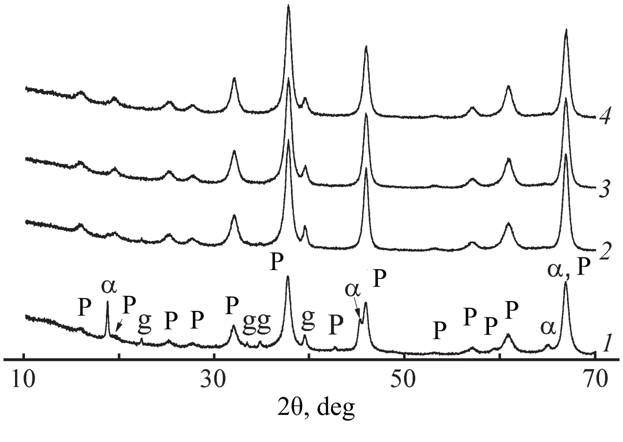

**Fig. 9.** XRD patterns of a mixture of lithium carbonate and aluminum hydroxide, activated during a varied time and calcined at 900°C for 2 h in air. Reflections: (P) $LiAl_5O_8$; (g) $\gamma$-$LiAlO_2$; (α) $\alpha$-$LiAlO_2$.

not yield boehmite (Fig. 7). Analysis of the behavior of lithium carbonate under heating of the activated mixture is difficult because of the broadening of the reflections of this compound. Broadened reflections of lithium pentaaluminate start to appear in the XRD pattern beginning at 600°C. Raising the temperature leads to a decrease in the width and increase in the intensity of the reflections associated with this compound. Raising the duration of the mechanical activation from 5 to 10 min weakly affects both the TG curves and the nature of phase transformations observed in the thermal treatment of a mechanically activated mixture (Figs. 4 and 8).

To study how the phase composition of the lithium aluminates being formed depends on the duration of the mechanical activation, we performed experiments on the thermal treatment of activated samples at 900°C for 2 h. As also shown by in situ experiments, the thermal treatment of an unactivated mixture of reagents yields a mixture containing $LiAl_5O_8$ with admixture of $\alpha$-$LiAlO_2$ and $\gamma$-$LiAlO_2$ (see the table, Fig. 9). The content of $\alpha$-$LiAlO_2$ and $\gamma$-$LiAlO_2$ impurity decreases with increasing duration of the mechanical activation, and upon a mechanical activation for 5 min, a single-phase lithium pentaaluminate is formed with specific surface area of 23 to 27 $m^2 g^{-1}$ (Fig. 1b). The average size $D$ of "primary" $LiAl_5O_8$ particles, calculated by the formula $S = 6/\rho S$, where ρ is the substance density (3.6 g $cm^{-3}$) and $S$ is the specific surface area, falls within the range 60–70 nm. Thus, the lithium pentaaluminate we synthesized is composed of submicrometer particles forming aggregates with micrometer and larger dimensions (Fig. 3). Noteworthy is the polymodal particle size distribution, which nearly coincides with the particle distribution in the mechanically activated mixture (Figs. 3a and 3b).

The available experimental data suggest the following scheme of processes occurring in the mechanochemical synthesis of lithium pentaaluminate. In the thermal treatment of an unactivated mixture of aluminum hydroxide and lithium carbonate in the temperature range 220–500°C, aluminum hydroxide decomposes to give a mixture of crystalline aluminum oxides $\gamma$-$Al_2O_3$ and $\chi$-$Al_2O_3$. Above 550°C, these oxides react with lithium carbonate to give $\alpha$-$LiAlO_2$, with lithium pentaaluminate formed at higher temperatures. The appearance of $\alpha$-$LiAlO_2$ in the first stage may occur for two reasons. In $\gamma$-$Al_2O_3$ and $\chi$-$Al_2O_3$, aluminum cations are predominantly in the octahedral coordination [11, 12].

Therefore, formation of α-$LiAlO_2$ in which all of the aluminum atoms are in octahedral oxygen coordination is presumably preferable to formation of $LiAl_5O_8$ in which the fraction of octahedrally coordinated aluminum is substantially smaller [14]. Another possible reason why α-$LiAlO_2$ is formed is the presence in the mixture of unactivated reagents of local regions with increased content of lithium carbonate. The appearance of an admixture of gamma-lithium monoaluminate is due to the phase transition of α-$LiAlO_2$ being formed to the γ-$LiAlO_2$ form [15].

The mechanical activation of the mixture leads to dispersion and mixing of the reagents, i.e., to a decrease in the percentage of local regions with increased content of lithium carbonate, which is a reason why the content of α-$LiAlO_2$ and γ-$LiAlO_2$ decreases with increasing activation duration. The mechanical activation of the mixture is accompanied not only by the dispersion and mixing of the reagents, but also by the amorphization of aluminum hydroxide and lithium carbonate. The thermal activation of a mixture activated for 5 min and more, which mostly contains X-ray-amorphous aluminum hydroxide, yields an X-ray-amorphous aluminum oxide in which the percentage of octahedrally coordinated aluminum is substantially lower, compared with crystalline aluminum oxides [15, 16]. In our opinion, the formation of $LiAl_5O_8$ in the interaction of X-ray-amorphous aluminum oxide with lithium carbonate is due to the less pronounced changes in the coordination environment of aluminum, compared with the formation of α-$LiAlO_2$, and just this is observed in the experiment.

## CONCLUSIONS

The preliminary mechanical activation of a mixture of aluminum hydroxide in the form of gibbsite and lithium carbonate in a planetary activator, followed by a thermal treatment in air at 900°C, makes it possible to obtain a single-phase lithium pentaaluminate with large specific surface area.

## ACKNOWLEDGMENTS

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