ISSN 0020-1685, Inorganic Materials, 2011, Vol. 47, No. 7, pp. 763–767. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.P. Isupov, O.A. Kharlamova, L.E. Chupakhina, M.R. Sharafutdinov, D.F. Khabibulin, O.B. Lapina, 2011, published in Neorganicheskie Materialy, 2011, Vol. 47, No. 7, pp. 849–853.

Mechanochemical Synthesis of γ-$LiAlO_2$ Studied by ^6Li and ^{27}Al NMR and Synchrotron X-Ray Diffraction

V. P. Isupov[a], **O. A. Kharlamova**[a], **L. E. Chupakhina**[a], **M. R. Sharafutdinov**[a], **D. F. Khabibulin**[b], **and O. B. Lapina**[b]

[a] *Institute of Solid-State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences,*
ul. Kutateladze 18, Novosibirsk, 630128 Russia

[b] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences,*
pr. Akademika Lavrent'eva 5, Novosibirsk, 630090 Russia

e-mail: isupov@solid.nsc.ru

Received September 6, 2010

Abstract—The structural transformations accompanying the mechanochemical synthesis of fine-particle γ-$LiAlO_2$ have been studied by ^6Li and ^{27}Al NMR and in situ X-ray diffraction. Mechanical activation of a mixture of aluminum hydroxide and lithium carbonate in an AGO-2 planetary mill results not only in size reduction, intermixing, and partial amorphization of the starting materials but also in the mechanochemical synthesis of a carbonate form of aluminum lithium hydroxide. Subsequent heat treatment of the mechanically activated mixture leads to the release of water and carbon dioxide molecules and the formation of an X-ray amorphous phase containing aluminum in octahedral and tetrahedral oxygen coordination. The X-ray amorphous material converts to gamma lithium aluminate through an intermediate phase.

DOI: 10.1134/S0020168511070120

INTRODUCTION

Fine-particle gamma lithium aluminate, γ-$LiAlO_2$, with a specific surface area above 10 m^2/g is used as an electrolyte support material for molten carbonate fuel cells [1], to modify the conductivity of lithium polymer electrolytes [2], and in lithium thermal batteries. γ-$LiAlO_2$ is commonly synthesized by a ceramic processing technique [3–5] or sol–gel process [6–8]. These approaches, however, have a number of serious drawbacks which limit their utility for large-scale production of fine-particle gamma lithium aluminate with a specific surface area large enough for the preparation of an electrolyte matrix support. In this context, there is currently considerable interest in commercially viable and environmentally friendly processes for the synthesis of fine-particle γ-$LiAlO_2$. As shown previously [9], phase-pure gamma lithium aluminate can be synthesized by heat-treating a mixture of aluminum hydroxide and lithium carbonate after mechanical activation in an AGO-2 laboratory-size planetary mill. The specific surface area of the gamma lithium aluminate thus prepared ranges from 8 to 25 m^2/g, depending on the activation and heat-treatment conditions. The process is environmentally safe and employs relatively inexpensive compounds: aluminum hydroxide and lithium carbonate [10]. The mechanism underlying the mechanochemical synthesis of gamma lithium aluminate is, however, essentially unexplored.

The purpose of this work was to study the structural changes accompanying the mechanochemical synthesis of gamma lithium aluminate by ^6Li and ^{27}Al NMR and in situ X-ray diffraction.

EXPERIMENTAL

The starting materials used were analytical-grade lithium carbonate and commercial aluminum hydroxide (gibbsite) manufactured at the Achinsk Alumina Refinery. A stoichiometric mixture of lithium carbonate and aluminum hydroxide was mechanically activated in an AGO-2 planetary mill at 40*g* for 10 min (200-ml steel vials, 5-mm-diameter steel balls, powder-to-ball weight ratio of 1 : 20). The structural changes caused by heat treatment of the mechanically activated mixture were studied in situ by synchrotron X-ray diffraction (SXRD). The process was run at the Difraktsionnoe Kino Station at the Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences, using the OD-3 linear position-sensitive detector (3328 channels, angular range of 30° (2θ), resolution of $\simeq 0.01°$, wavelength of 1.522 Å). The mixture was heated in air at a rate of $\simeq$ 10°C/min.

The products of the reaction between the mechanically activated aluminum hydroxide and lithium carbonate in air were characterized by ^6Li and ^{27}Al NMR. In our experiments, we used lithium carbonate containing about 50 at % ^6Li. NMR spectra were taken on a Bruker Avance 400 spectrometer using magic angle spinning at 10 kHz. Samples of the mechanically activated mixture were heated in air at a rate of 10°C /min to a preset temperature in an SNOL furnace, then withdrawn, and stored in hermetically sealed ampules until measurements. Peak positions were determined relative to the NMR signals of aqueous aluminum nitrate and lithium chloride.

RESULTS AND DISCUSSION

As shown previously [9], the activation of a mixture of aluminum hydroxide and lithium carbonate in an AGO-2 planetary mill leads not only to size reduction but also to aluminum hydroxide amorphization and the formation of a carbonate form of aluminum lithium hydroxide. After milling for 10 min, the double hydroxide is X-ray amorphous. Like in an earlier study, the XRD pattern of the milling products shows broadened reflections from lithium carbonate, whereas the reflections from aluminum hydroxide are extremely weak (Fig. 1). The ^{27}Al NMR spectrum of the mechanically activated mixture (Fig. 2) shows a band at a chemical shift of 7 ppm, characteristic of aluminum cations in octahedral oxygen coordination [11]. The octahedral coordination of the aluminum in the mechanically activated mixture lends support to the assumption that milling converts some of the aluminum hydroxide to an X-ray amorphous state, whereas the rest is incorporated into the carbonate form of aluminum lithium hydroxide, $[LiAl_2(OH)_6]_2CO_3 \cdot nH_2O$ ($Li-Al-CO_3$).

Heating the mechanically activated mixture of aluminum hydroxide and lithium carbonate to 200°C removes the water from the X-ray amorphous aluminum hydroxide and $Li-Al-CO_3$, without significant changes in XRD patterns (Fig. 1) or ^{27}Al or ^{6}Li NMR spectra (Figs. 2, 3).

Subsequently raising the heat-treatment temperature to above 200°C leads to a gradual decrease in the intensity of reflections from lithium carbonate, which are essentially missing at a heat-treatment temperature of 550°C, indicating that the amount of this reactant gradually decreases. At heat-treatment temperatures above 550°C, the reaction product is essentially X-ray amorphous.

With increasing temperature, the ^{27}Al NMR band at a chemical shift of 68–70 ppm, arising from tetrahedrally coordinated aluminum [11], gradually grows. As a result, the bands due to octahedrally and tetrahedrally coordinated aluminum in the spectrum of the X-ray amorphous material are comparable in intensity.

Heating changes the shape of the bands in the ^{6}Li NMR spectrum of the mechanically activated mixture, which points to changes in the coordination of the lithium cations (Fig. 3). In particular, the NMR spectrum of the sample prepared at 550°C, that is, under the conditions corresponding to the formation of an X-ray amorphous phase, shows a rather strong shoulder, indicating the presence of a band at a chemical shift of –0.3 to –0.4 ppm, due to lithium in tetrahedral oxygen coordination [12].

Raising the heat-treatment temperature to 600–650°C gives rise to three broad XRD lines, at $2\theta = 20°$–25°, 32.5°–35°, and 35°–37°. Comparison of these reflections with those from the best known crystalline forms of lithium aluminate (α, β, and γ) suggests the following: First of all, they differ dramatically in position from those of the low-temperature phase α-$LiAlO_2$ (Fig. 4). The position of the first reflection coincides with that of the 101 reflection from γ-$LiAlO_2$ and differs little from those of the two closely spaced, strong reflections from β-$LiAlO_2$: 110 and 011 (Fig. 4). The second reflection is identical in position to the 102 reflection from γ-$LiAlO_2$ and the 120 reflection from β-$LiAlO_2$. At the same time, the third reflection differs rather significantly in position from its nearest neighbors: 200 and 002 of β-$LiAlO_2$ and 200 of γ-$LiAlO_2$.

The ^{27}Al NMR spectrum of the sample prepared at 650°C shows an increased intensity of the band due to tetrahedrally coordinated aluminum.

The ^{6}Li NMR spectrum shows a marked reduction in the intensity of the band at a chemical shift of –0.9 ppm and a sharp rise in the intensity of the band at –0.3 ppm. Thus, the NMR data indicates that the formation of an intermediate phase increases the percentages of aluminum and lithium in tetrahedral oxygen coordination.

At heat-treatment temperatures above 650°C, the first two peaks in the XRD patterns narrow down, without changes in their position. The third peak shifts to smaller angles with increasing temperature. In addition, a new reflection emerges, identical in position to the 200 reflection from γ-$LiAlO_2$, and its intensity gradually increases. These changes, along with the emergence of three peaks close in position to the 110, 111, and 211 reflections from gamma lithium aluminate, indicate the formation of gamma lithium aluminate, which is well seen at 850°C. Note that the XRD patterns show, in addition to the reflections from gamma lithium aluminate, weak reflections from α-$LiAlO_2$, indicating that, under the experimental conditions of this study, this phase is present as an impurity.

^{27}Al and ^{6}Li NMR data lend support to the above XRD data. In particular, the ^{27}Al and ^{6}Li NMR spectra of the sample prepared at 850°C are dominated by bands of aluminum and lithium in tetrahedral oxygen coordination (Fig. 2), characteristic of γ-$LiAlO_2$.

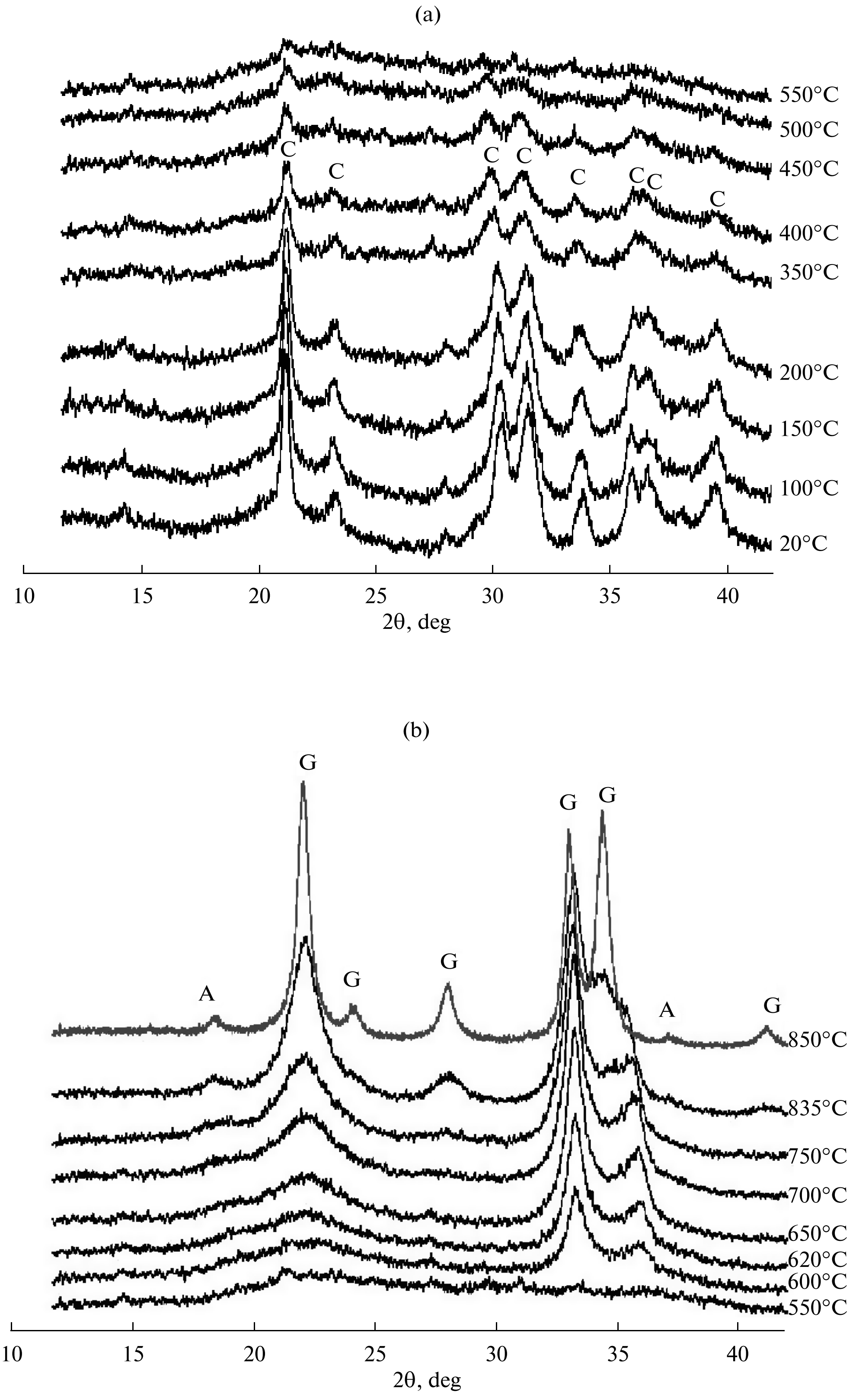

Fig. 1. In situ XRD data (CuK_α radiation) for a mechanically activated mixture of aluminum hydroxide and lithium carbonate heated in air at a rate of 10°C/min; C = Li_2CO_3, A = α-$LiAlO_2$, G = γ-$LiAlO_2$.

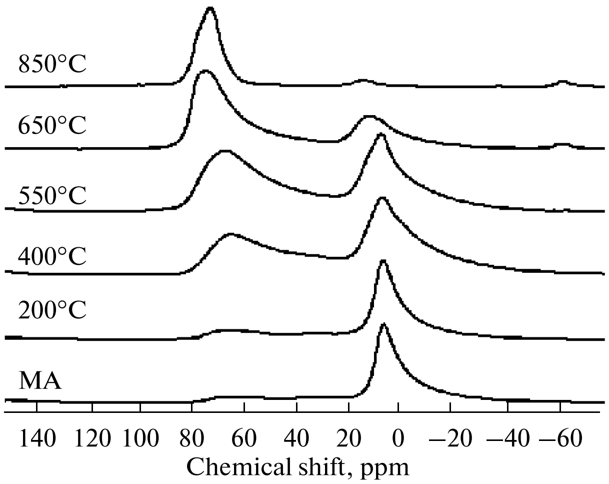

Fig. 2. ^{27}Al NMR spectra of a mechanically activated mixture of aluminum hydroxide and lithium carbonate heated in air at different temperatures.

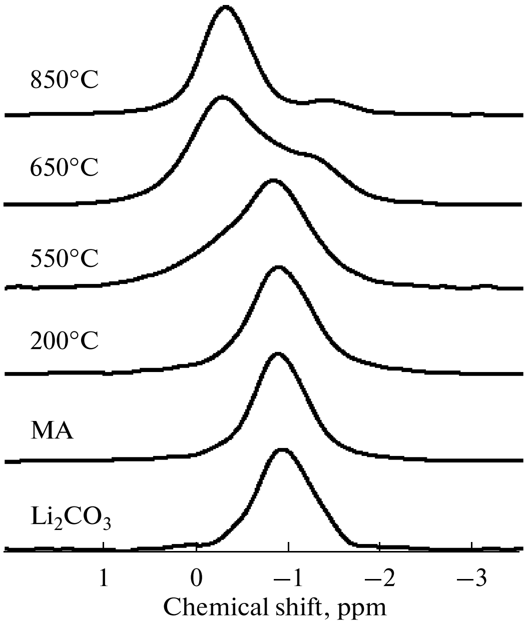

Fig. 3. ^{6}Li NMR spectra of a mechanically activated mixture of aluminum hydroxide and lithium carbonate heated in air at different temperatures.

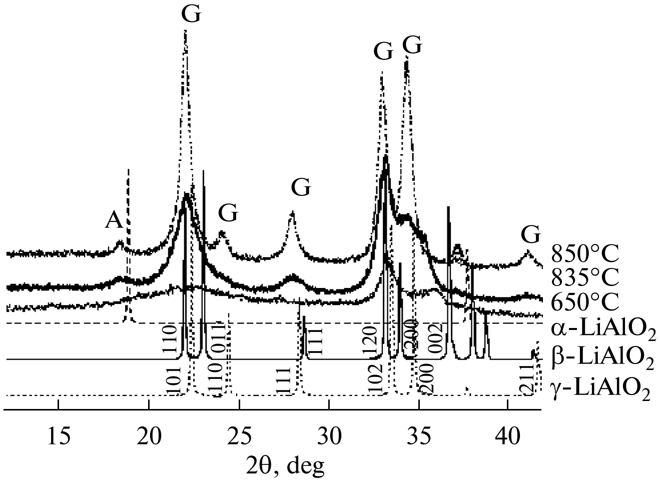

Fig. 4. Comparison of the XRD patterns (Cu K_α radiation) of the mechanically activated mixture heated to 650, 835, and 850°C and literature data for α-, β-, and γ-$LiAlO_2$; A = α-$LiAlO_2$, G = γ-$LiAlO_2$.

CONCLUSIONS

Mechanical activation of a mixture of aluminum hydroxide and lithium carbonate causes not only changes in the state of the starting materials (size reduction, intermixing, and amorphization) but also molecular-scale mixing, resulting in the formation of a carbonate form of aluminum lithium hydroxide. Heat treatment of the mixture leads to the release of water and carbon dioxide molecules and the formation of an X-ray amorphous phase containing aluminum in octahedral and tetrahedral oxygen coordination. The formation of crystalline gamma lithium aluminate from the X-ray amorphous material occurs through the formation of an intermediate phase containing aluminum and lithium in tetrahedral oxygen coordination. According to the present XRD data, this phase differs in structure from the lithium aluminates known in the literature.

ACKNOWLEDGMENTS

This work was supported by the Siberian Branch of the Russian Academy of Sciences (Siberia's Lithium Interdisciplinary Integrated Research Project no. 29) and the Chemistry and Materials Science Division of the Russian Academy of Sciences (project no. 5.7.8).

REFERENCES

1. Molten Carbonate Fuel Cells, in *Fuel Cell Handbook,* Morgantown: DOE/NETL, 2002, 6th ed., chapter 6.
2. Morita, M., Fujisaki, T., Yoshimoto, N., and Ishikawa, M., Ionic Conductance Behavior of Polymeric Composite Solid Electrolytes Containing Lithium Aluminate, *Electrochim. Acta,* 2001, vol. 46, pp. 1565–1569.
3. Bertaut, F., Delapalm, A., Bassi, G., et al., Structure of γ-$LiAlO_2$, *Bull. Soc. Fr. Mineral. Cristallogr.,* 1965, no. 88, pp. 103–108.
4. Lehmann, H.A. and Hesselbarth, H., Über eine neue Modifikation des $LiAlO_2$, *Z. Anorg. Allg. Chem.,* 1961, no. 313, pp. 117–124.
5. Kinoshita, K., Sim, J.W., and Ackerman, J.P., Preparation and Characterization of Lithium Aluminate, *Mater. Res. Bull.,* 1978, no. 13, pp. 445–455.

6. Hirano, S., Hayahi, T., and Kageyama, T., Synthesis of $LiAlO_2$ Powder by Hydrolysis of Metal Alkoxides, *J. Am. Ceram. Soc.,* 1987, vol. 70, no. 3, pp. 171–174.
7. Kwon, S.W. and Kim, E.H., The Formation of Phase Pure Lithium Aluminate from the Bulky Lithium and Aluminium Alkoxides, *J. Mater. Sci. Lett.,* 1999, no. 18, pp. 931–933.
8. Kadokura, H., Umezaki, H., Murakami, H., and Mizoe, T., Jpn. Patent 4704266.
9. Kharlamova, O.A., Mitrofanova, R.P., and Isupov, V.P., Mechanochemical Synthesis of Fine-Particle γ-$LiAlO_2$, *Neorg. Mater.,* 2007, vol. 43, no. 6, pp. 732–737 [*Inorg. Mater.* (Engl. Transl.), vol. 43, no. 6, pp. 645–650].
10. Kharlamova, O.A., Mitrofanova, R.P., and Isupov, V.P., RF Patent 2 347 749, *Byull. Izobret.,* 2009, no. 6,
11. Stewart, F.F., Stebbins, J.F., Peterson, E.S., et al., Mobility and Relaxation Determinations of Lithium in Lithium Aluminate Ceramics Using Solid-State NMR Spectroscopy, *Chem. Mater.,* 1995, no. 7, pp. 363–367.
12. Hou, X. and Kirkpatrick, R.J., Thermal Evolution of the Cl–$LiAl_2$ Layered Double Hydroxide: A Multinuclear MAS NMR and XRD Perspective, *Inorg. Chem.,* 2001, vol. 40, pp. 6397–6404.