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Influence of hydrothermal conditions on the phase transformations of amorphous alumina

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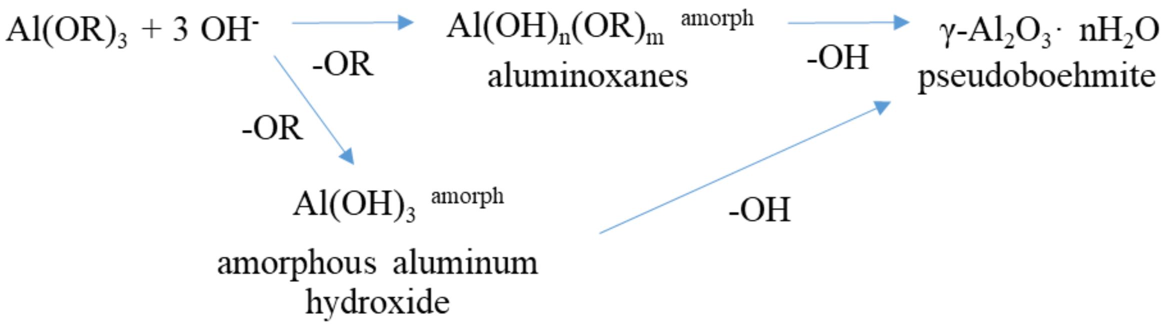
1. General information

Monophasic amorphous alumina was obtained by heat treating in muffle furnace at 550 °C during 2 h (heating rate 5 °C/min). Precursor of amorphous alumina was the product of aluminum isopropoxide hydrolysis by water vapor and included >90 wt% of amorphous hydroxide. Polyaluminoxanes, stabilized in aluminum monohydroxide (boehmite), and amorphous aluminum hydroxide were formed during hydrolysis of aluminum alkoxides according to the following scheme:

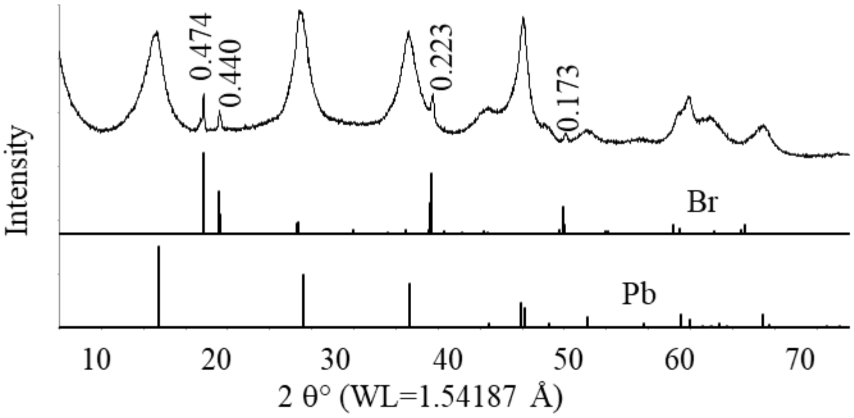


Amorphous aluminum hydroxide was transformed into amorphous alumina after heat treatment at T <550 °C, aluminoxanes and boehmite were converted analogously to γ-Al_2O_3.

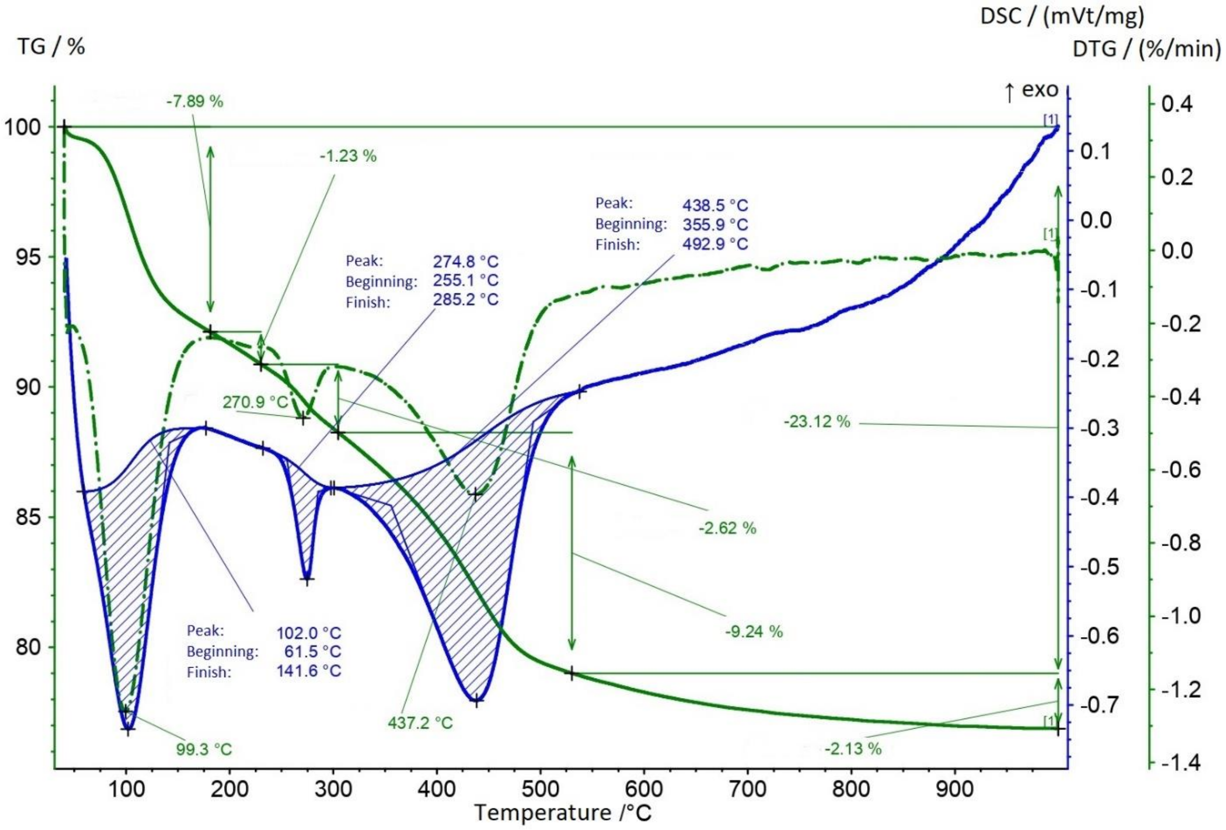
2. Phase composition of hydrothermal treatment product of amorphous alumina

Hydrothermal treatment of amorphous alumina was carried out at T=110–150 °C in water solution at saturated water vapor pressure 0.14–0.48 MPa for 0–360 min. Samples was collected in a heating mode of autoclave reactor for 15 min, when the phase transformation was beginning, and in isothermal mode after reaching the temperature required. pH value of the amorphous alumina suspension in water was 8.1. Hydrothermal modification was carried out using a BüchiGlasUster ‘Limbo li’ autoclave (Switzerland) with automatic temperature and pressure control in 250 ml steel reactor. Alumina to water ratio was 1 : 5, the maximal autoclave filling out was up to 70 %.

Pseudoboehmite (Pb), boehmite and bayerite (Br) are identified on diffractograms by their corresponding diffraction lines [Figure S1(*a*)].

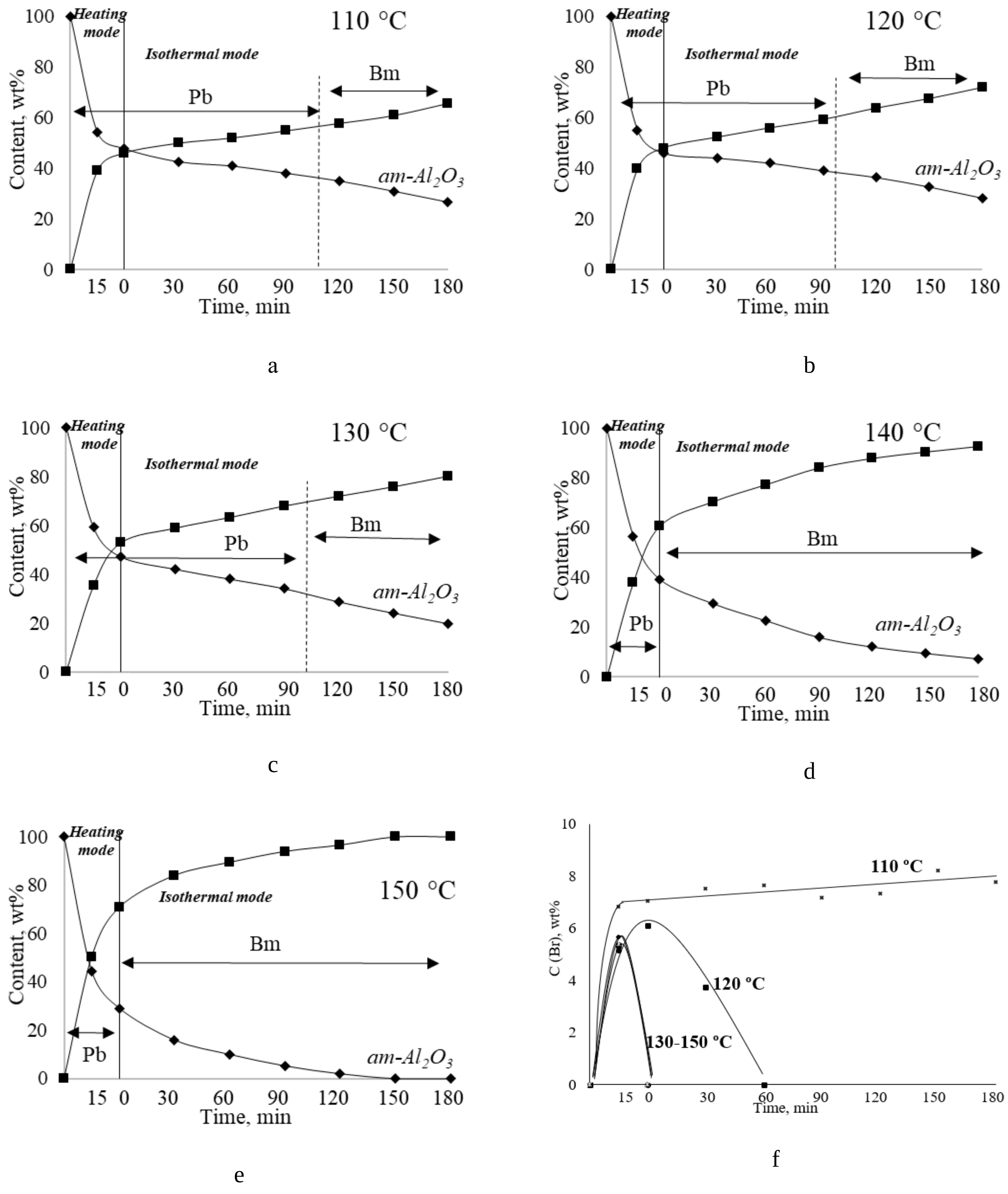


(*a*)



(*b*)

Figure S1 (*a*) Diffractogram and (*b*) TG–DSC data for the hydrothermal treatment products (*T* = 110 °C, *τ* = 150 min).



a

b

c

d

e

f

Figure S2 Kinetic curves of amorphous alumina transformation and aluminum hydroxide formation at different temperature under hydrothermal conditions.

The phase composition of samples was determined using X-ray powder diffraction (XRPD) by a MiniFlex 600 diffractometer (Rigaku, Japan) equipped with a D/teX Ultra detector. γ-Al_2O_3 was identified on the diffraction lines with distances $d/I_{(440)} = 0.139$ nm, $d/I_{(115)} = 0.152$

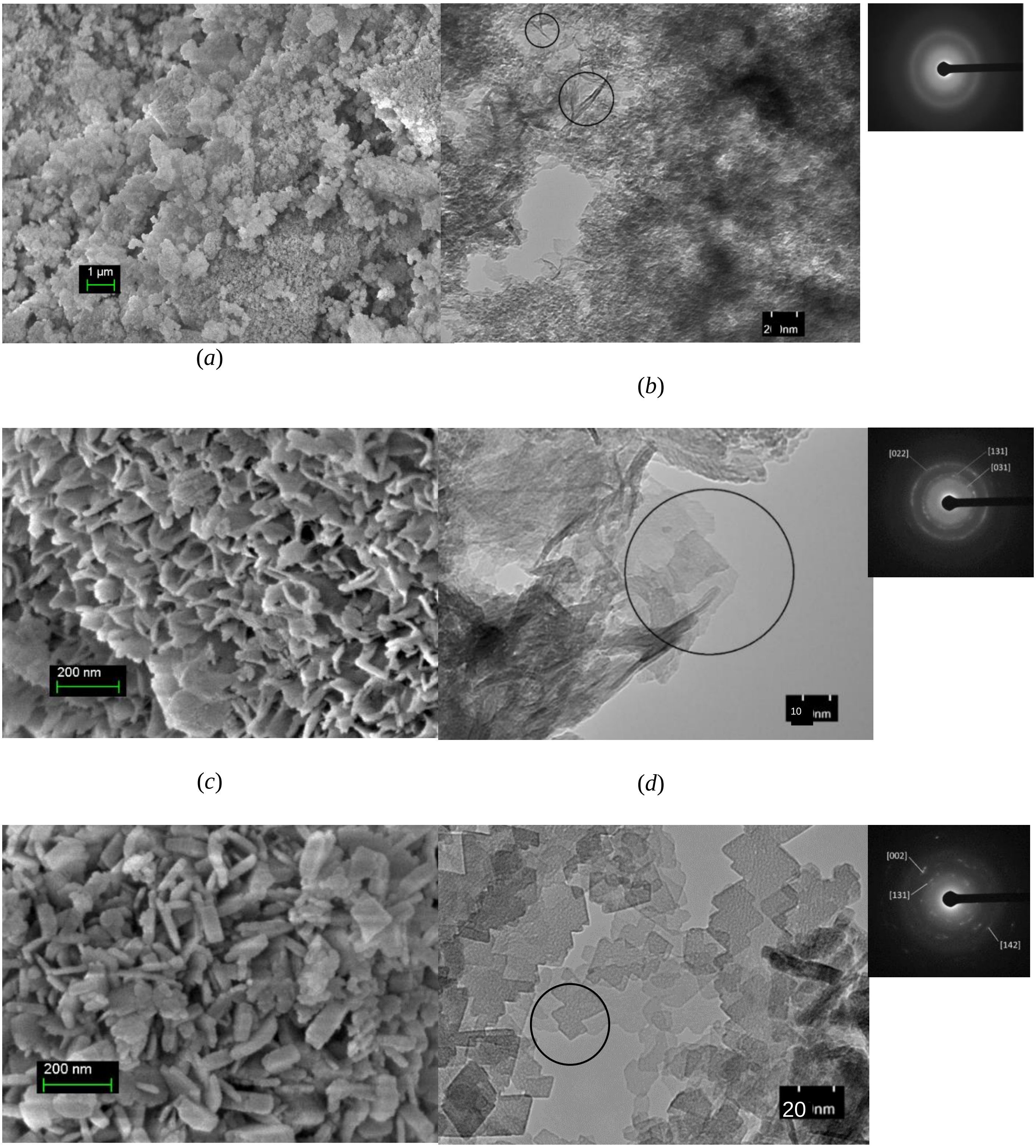
nm, $d/l_{(004)}$ = 0.198 nm, $d/l_{(222)}$ = 0.228 nm, $d/l_{(113)}$ = 0.231 nm, $d/l_{(220)}$ = 0.280 nm, $d/l_{(111)}$ = 0.456 nm (JCPDS Card 00-010-0425), boehmite and pseudoboehmite: $d/I_{(020)}$ = 0.611 nm, $d/I_{(120)}$ = 0.316 nm, $d/I_{(031)}$ = 0.235 nm, $d/I_{(200)}$ = 0.185 nm, $d/I_{(151)}$ = 0,166 nm, $d/I_{(231)}$ = 0.145 nm, $d/I_{(002)}$ = 0.143 nm, $d/I_{(171)}$ = 0.138 nm, $d/I_{(251)}$ = 0.131 nm, $d/I_{(202)}$ = 0.113 nm (JCPDS Card 00-021-1307), bayerite: $d/I_{(002)}$ = 0.474 nm, $d/I_{(110)}$ = 0.440 nm, $d/I_{(020)}$ = 0.436 nm, $d/I_{(112)}$ = 0.322 nm, $d/I_{(022)}$ = 0.321 nm, $d/I_{(122)}$ = 0.272 nm, $d/I_{(004)}$ = 0.237 nm, $d/I_{(202)}$ = 0.224 nm, $d/I_{(132)}$ = 0.223 nm, $d/I_{(024)}$ = 0.208 nm, $d/I_{(222)}$ = 0.200 nm (PDF Card 01-076-7848).

The phase concentrations were determined using the thermal analysis (TA; Netzsch STA–449C Jupiter, Selb, Germany). The TA was carried out in a way that is capable of recording the thermogravimetric (TG), derivative scanning calorimetry (DSC) and differential thermal analysis (DTA) curves simultaneously. The samples were heated in the temperature range of 30–1000 °C at the heating rate of 10 °C min^{-1} in an Ar flow. Concentration of aluminum hydroxides was calculated from the amount of water released during the aluminum hydroxides dehydration and dehydroxylation. Amount of interlayer water for pseudoboehmite and boehmite was calculated as the following: n = 1.00–1.19 mol H_2O/mol Al_2O_3 for boehmite; n = 1.20–2.00 mol H_2O/mol Al_2O_3 for pseudoboehmite and n = 3.00 mol H_2O/mol Al_2O_3 for bayerite.

Bayerite was identified on the DSC curves by water release in the II endothermal effect area (221–286 °C) when it was transformed into η-Al_2O_3 (85.0 wt%) and boehmite (15.0 wt%). Pseudoboehmite (n = 1.20–1.39 mol H_2O/mol Al_2O_3) and boehmite (n = 1.03–1.18 mol H_2O/mol Al_2O_3) are identified by the III endothermal effect (332–534 °C, T_p (temperature peak) = 419–438 °C and 349–507 °C, T_p = 438–490 °C) of dehydration to γ-Al_2O_3 [Figure S1(*b*)].

3. Morphology of the hydrothermal treatment products

Morphology of samples was analyzed by scanning and transmission electron microscopy. The measurements by scanning electron microscopy (SEM) were carried out using field-emission high-resolution scanning electron microscope (Merlin Carl Zeiss, Germany). Observation photo of the sample surface was obtained at accelerating voltage of incident electron 5 kV and current probe 300 pA to minimize the sample modification. The transmission electron microscopy (TEM) was carried out using an electron microscope HT7700 (Hitachi High Technology, Japan). During a sample preparation, 10 μl of the sample suspension was placed on a 3 mm copper mesh with a formvar/carbon substrate and dried at the room temperature. The analysis was performed at an accelerating voltage of 80 kV in the TEM mode.



(*a*)

(*b*)

(*c*)

(*d*)

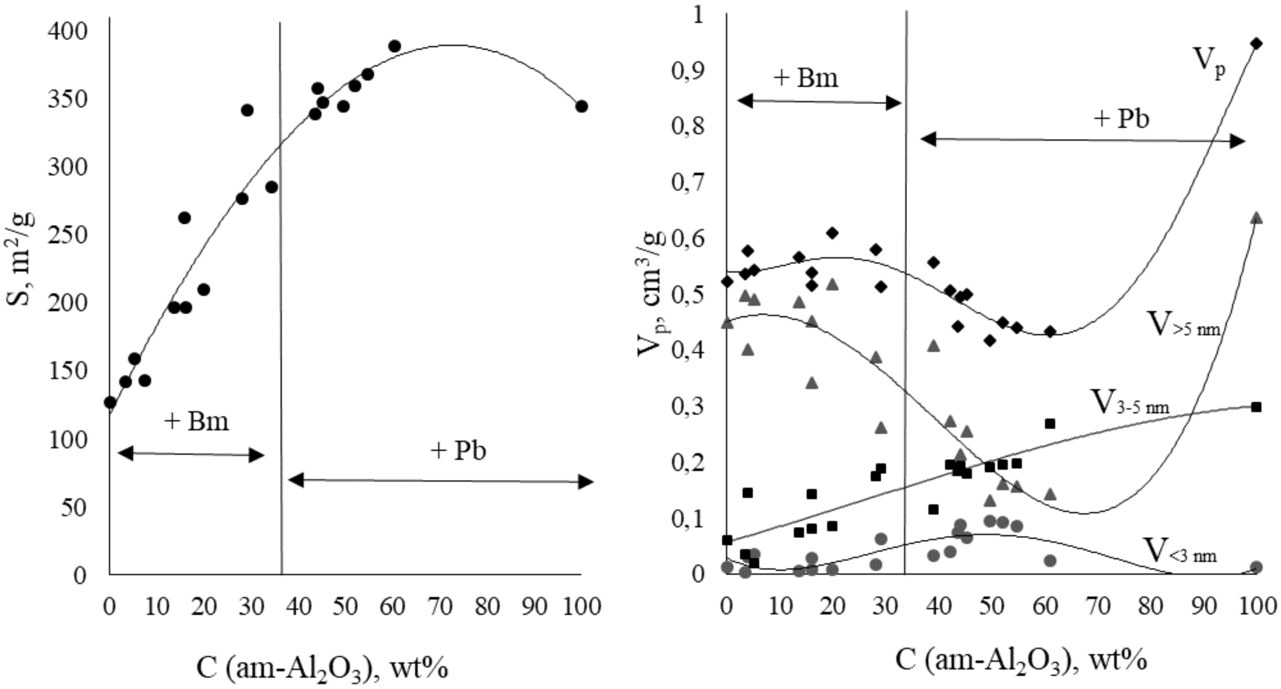
(*e*)

(*f*)

Figure S3. SEM and TEM images of (*a*,*b*) amorphous alumina and its hydrothermal products in isothermal mode at (*c*,*d*) 110 °C/0 min (C_{Pb} = 45.3 wt%) and (*e*,*f*) 150 °C /120 min (C_{Bm} = 96.6 wt%).

4. Porous system of the hydrothermal treatment products

Porous system of the hydrothermal treatment products of amorphous alumina was analyzed by low-temperature nitrogen adsorption.

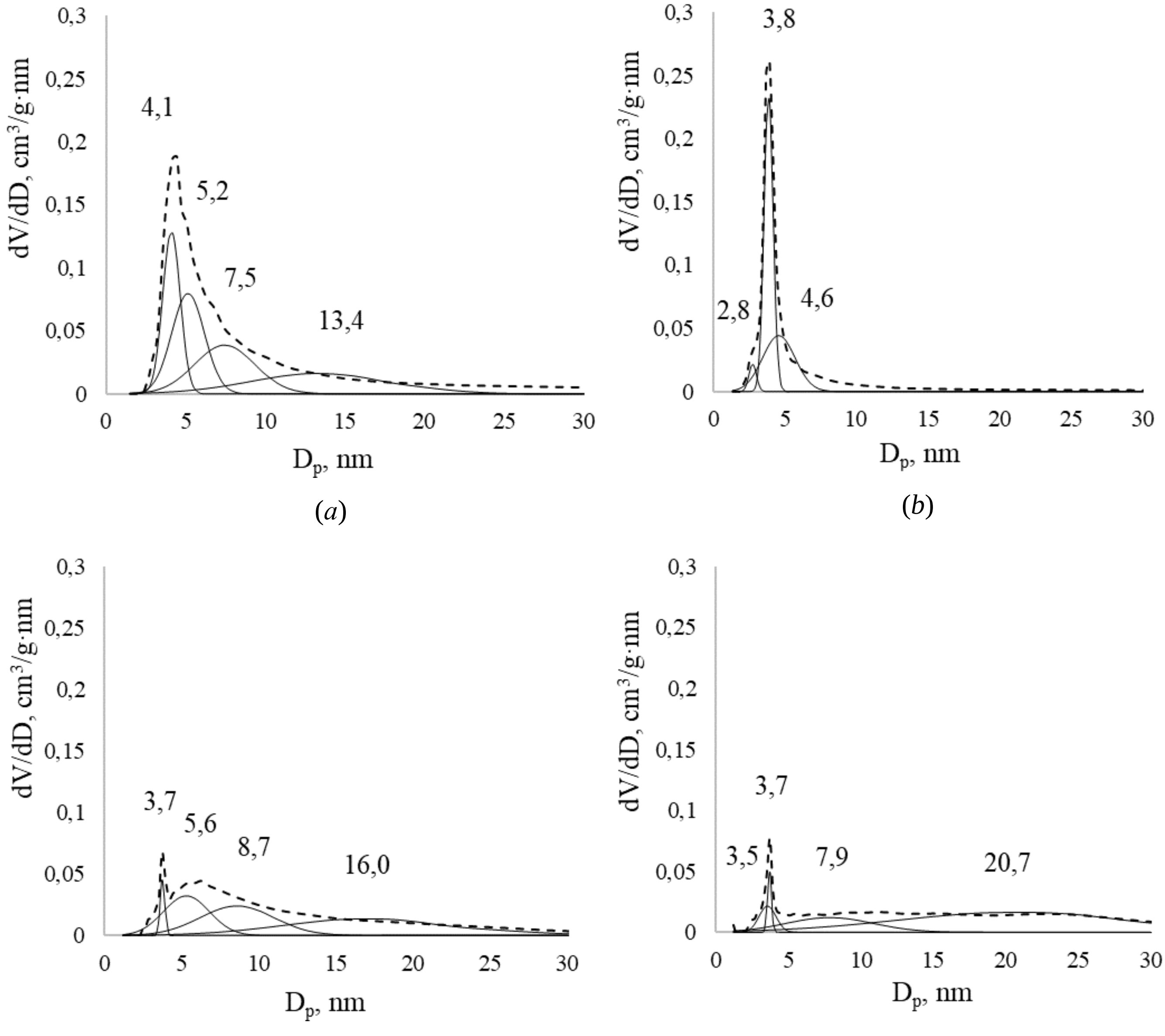


(*a*) (*b*)

Figure S4 (*a*) Specific surface area *S* and (*b*) pore volume V_p of aluminum monohydroxides formed under hydrothermal condition from amorphous alumina.

Specific surface area *S* (calculated by the Brunauer–Emmett–Teller method) and pore volume V_p (calculated from the last point of the isotherm) were determined using ASAP 2460 pore analyzer (Micromeritics, USA). Adsorption isotherms were obtained at −196 °C (77 K) after the degassing of samples at 150–300 °C under the residual pressure of 0.013 Pa. The meso- and micropore volumes distributions over the pore diameters were calculated from the curve of desorption isotherm using the standard Barrett–Joyner–Halenda (V_{BJH}) and Horwath–Kavazoe (V_{HK}) methods.

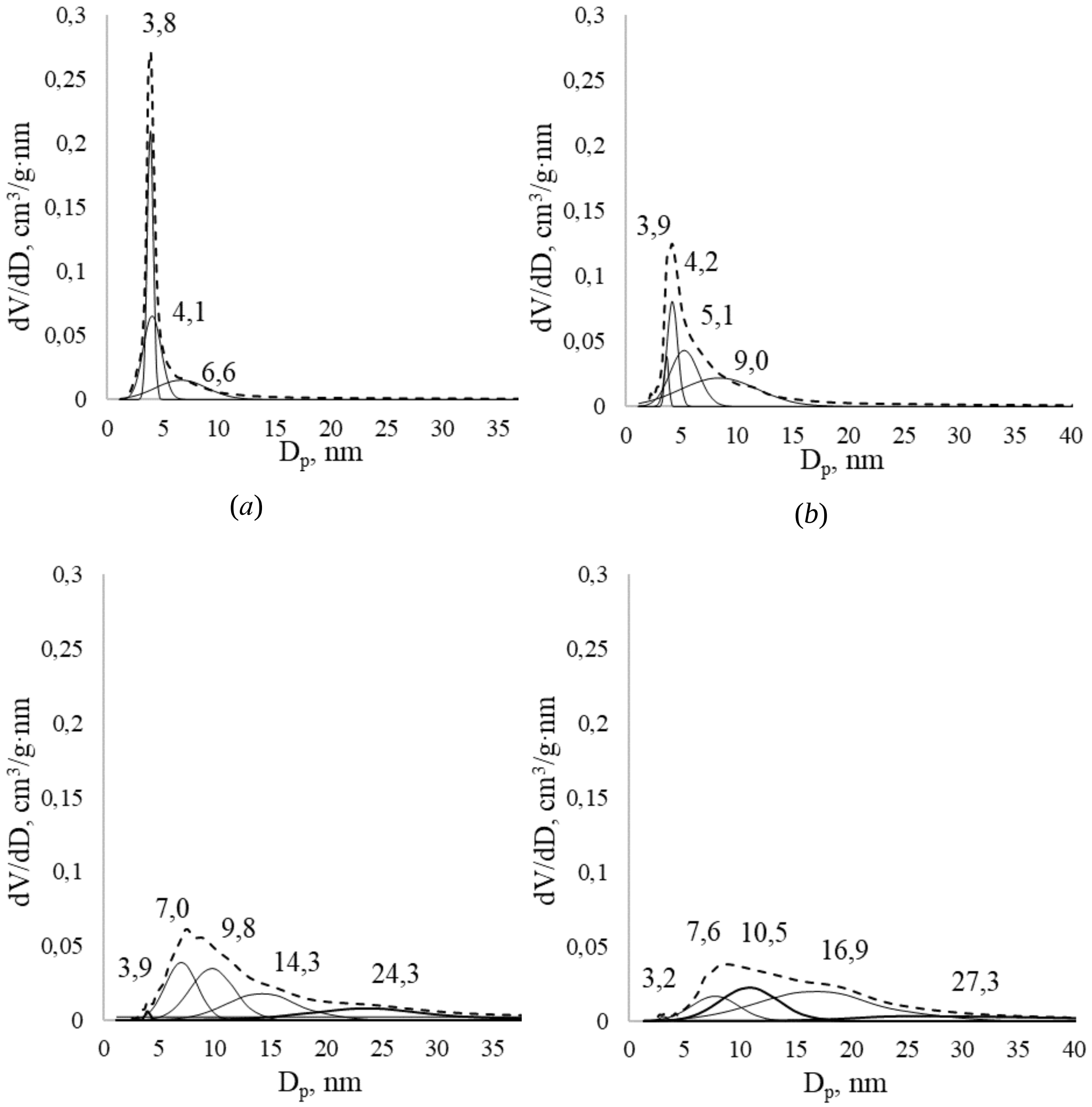
Pores with 3.8 nm diameter of the hydrothermal treatment products are probably inhered by amorphous alumina due to its partial disaggregating. The pore volume increased to 0.55 cm^3 g^{-1} with growth of hydrothermal treatment time, temperature and pseudoboehmite concentration to ~56 wt%. It is associated with pore volume (<5 nm diameter) increasing in ~1.6 times area because of pseudoboehmite particles coarsening before its crystallization to boehmite.



(*a*) (*b*)

(*c*) (*d*)

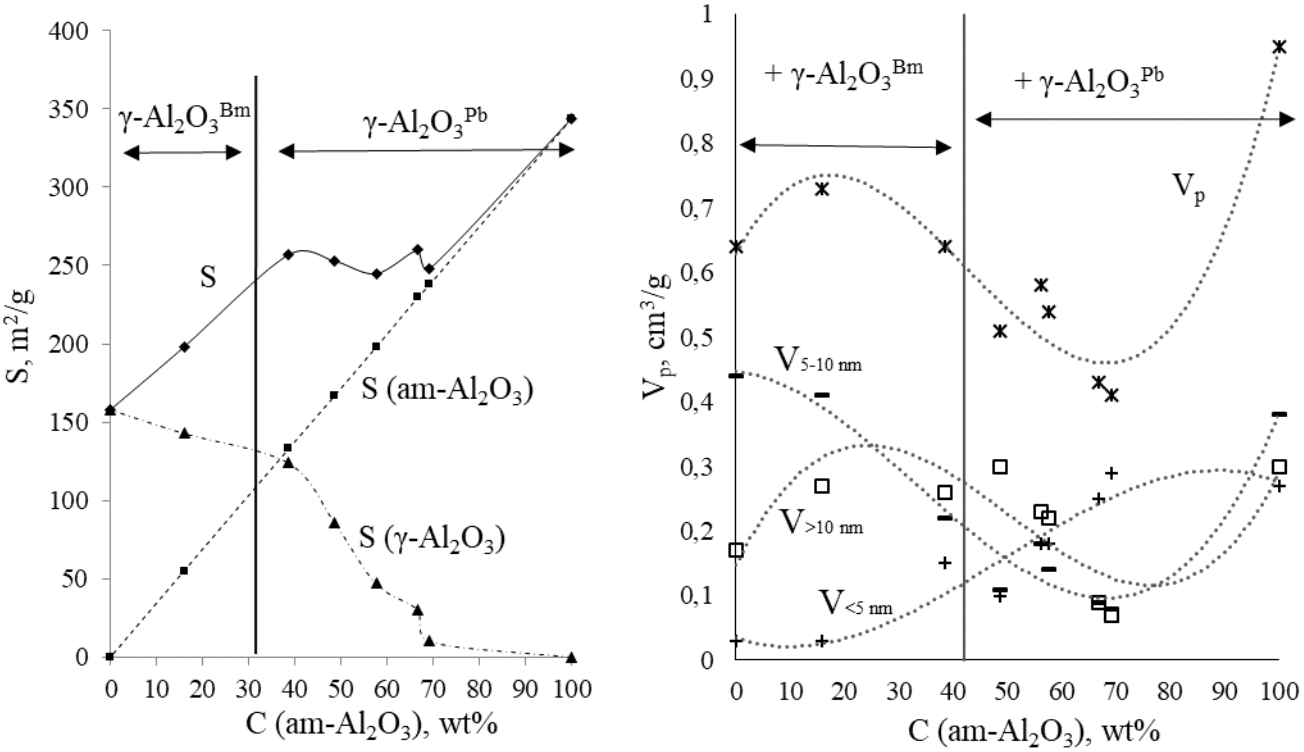
Figure S5 Curves of pore volume distribution of (*a*) amorphous alumina as well as its hydrothermal treatment products (*b*) at 110 °C for 15 min, (*c*) at 140 °C for 90 min and (*d*) at 150 °C for 180 min, with decompounding of Gaussian parts.



(*a*) (*b*)

(*c*) (*d*)

Figure S6 Pore volume distribution of aluminaobtained from hydrothermal treatment products containing *ca.* (*a*) 70, (*b*) 40, (*c*) 16 and (*d*) 0 wt% of am-Al_2O_3, with decompounding of Gaussian parts.



(*a*) (*b*)

Figure S7 Specific surface area of (*a*) individual parts and (*b*) pore volume of alumina obtained from hydrothermal treatment products.

5. Acid properties of alumina obtained from hydrothermal treatment products

The surface acidity of samples was analyzed by the method of temperature-programmed desorption of ammonia (TPD-NH_3) using a flow-type instrument with a thermal conductivity detector ChemBet Pulsar (Quantachrome, USA). Before the ammonia adsorption, the sample was degassed by heating up to 550 °C in a He flow. Temperature-programmed desorption of ammonia was carried out from room temperature to 700 °C at a rate of 10 °C min^{-1}. Calculations of TPD-NH_3 data on the distribution of acid sites were performed according to the method given in the research.

Acid sites are divided on weak (E_d < 110 kJ mol^{-1}), medium (E_d = 110–142 kJ mol^{-1}) and strong (E_d ≥142 kJ mol^{-1}) depending on the temperature and activation energy (E_d).

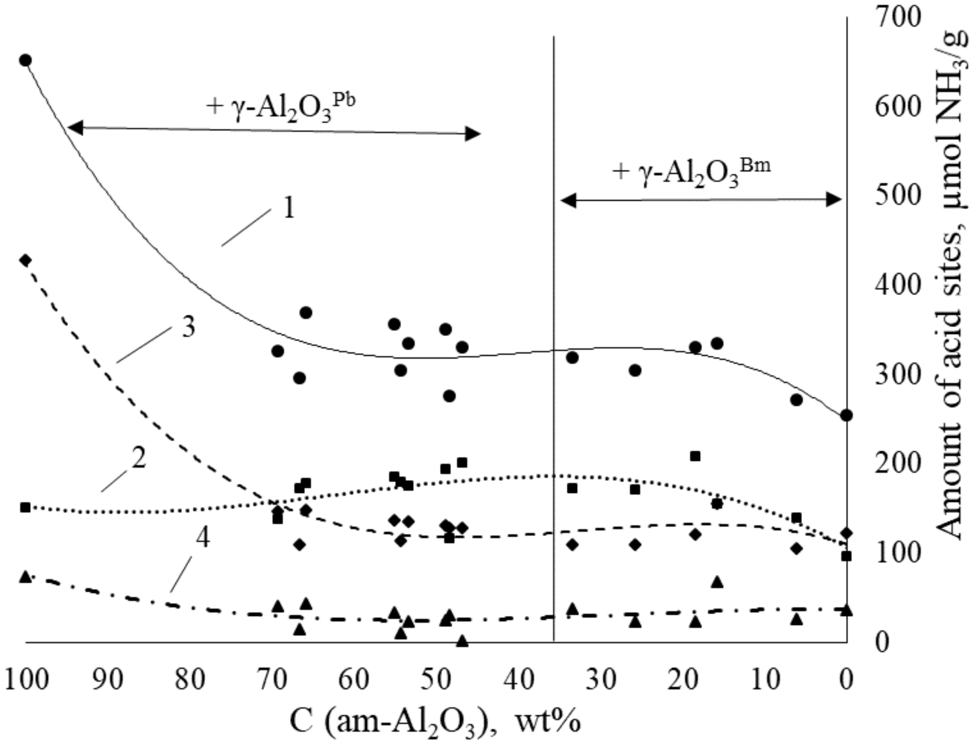


Figure S8 Amount of acid sites of amorphous alumina and alumina synthesized from hydrothermal treatment products.

Thus, pseudoboehmite, boehmite and bayerite (up to 8 wt%) are obtained by hydrothermal treatment of amorphous alumina at T = 110–150 °C and saturated water vapour pressure during 3 h. Amorphous alumina → pseudoboehmite (up to ~40 wt%) transition is accompanied by increasing of specific surface area (up 344 to 388 m^2 g^{-1}) and decline of pore volume (up 0.95 to 0.41 cm^3 g^{-1}) because of thin pore with 2.8–3.8 nm diameter of pseudoboehmite particles. Further, boehmite is crystallized to 100 wt% with growth of pore volume to 0.50–0.62 cm^3 g^{-1} due to increasing of pore volume with >5 nm diameter. Hydrothermal treatment products, namely pseudoboehmite and boehmite, are transformed to γ-$Al_2O_3^{Pb}$ and γ-$Al_2O_3^{Bm}$ after heat treatment at 550 °C during 3 h. Amorphous alumina is stabilized up to ~700 °C. γ-$Al_2O_3^{\text{Пb}}$ inherits thin pores from pseudoboehmite with downtrend of specific surface area from 344 to 248 m^2 g^{-1} and pore volume from 0.95 to 0.41–0.65 cm^3 g^{-1}. Pore system of alumina synthesizing from boehmite is differed by growth of total pore volume to 0.73 cm^3 g^{-1} because of pore coarsening and lowering of S to 198 m^2 g^{-1}. Total amount of acid sites on the alumina surface is correlated with its specific surface area. Medium acid sites (E_d = 110–142 kJ mol^{-1}) are exceeded (47 %) in amorphous alumina. γ-$Al_2O_3^{Pb}$ and γ-$Al_2O_3^{Bm}$ are source of weak acid sites (E_d <110 kJ mol^{-1}). Total amount of acid sites of alumina synthesized from hydrothermal treatment products by heat treatment at 550 °C is decreased from 652 (amorphous alumina) to 255 μmol NH_3 g^{-1} (γ-$Al_2O_3^{Bm}$).