

INORGANIC SYNTHESIS  
AND INDUSTRIAL INORGANIC CHEMISTRY

# Hydrothermal Synthesis of Magnesium Silicate Montmorillonite for Polymer–Clay Nanocomposites

O. Yu. Golubeva, E. N. Korytkova, and V. V. Gusarov

*Grebenshchikov Institute for Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia*

Received September 7, 2004

**Abstract**—Conditions of hydrothermal synthesis of magnesium silicate montmorillonite  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  with a particle size of 50–100 nm are optimized, including the temperature, initial chemicals, reaction medium, and run duration.

At present, synthesis of hybrid polymer–inorganic nanocomposites appears to be one of the most effective ways in developing novel structural materials. A steadily growing interest in nanocomposites is stimulated by their improved physical and mechanical characteristics as compared to micro- and macrocomposites containing the same or even larger amounts of an inorganic filler.

Interest in polymer–inorganic nanocomposites based on layered silicates has quickened since 1987, when a series of works on Nylon–clay hybrids were published by the Toyota Research Center [1]. It was demonstrated that small additions of layered minerals, particularly montmorillonite, significantly enhance the thermal resistance and mechanical characteristics of the polymer.

Later on polymeric nanocomposites with layered silicates as fillers were intensively studied [2–6]. Polymer–silicate nanocomposites were found to be characterized by increased strength, thermal and chemical resistance, and ionic conductivity and by lower thermal expansion coefficient and gas permeability as compared to the initial polymer. Several characteristics were also improved, such as the flame propagation resistance and barrier action, which could not be realized with any other filler [7]. It is significant that such improvements of properties were not accompanied by noticeable increase in the density or decrease in the light transmission [8].

The possibility of improvement of a series of performance characteristics stimulated more extensive applications of polymer–inorganic materials in such areas as motor-car construction, light industry, electronics, and aerospace industry [9].

In the works devoted to synthesis and characterization of polymer–inorganic nanocomposites, such polymers as polyester, polyurethane, polystyrene, polypropylene, polyethylene, polybutadiene resin, polyaniline, and many others were used [10]. However, in all cases, practically the only material, montmorillonite, representing a layered silicate, was used a filler.

Layered silicates are very convenient materials for fabrication of nanocomposites (nanocomposite is a composite material in which a filler dispersed in the polymer matrix has at least one dimension of nanometer size). Silicate layers, being about 1 nm thick and 100–1000 nm wide, have highly developed surface capable of interacting with the polymer matrix. The particle size distribution and interaction of the silicate layers with the polymer matrix control the performance characteristics of the resulting composite. Minerals belonging to the montmorillonite group, in their turn (by virtue of their structural features), are the most suitable layered silicates for nanocomposites.

Montmorillonites are natural clay minerals with the general formula  $(\text{Na}, \text{Ca}, \text{K})_{x+y}(\text{Si}_{y-x}\text{Al}_x)(\text{Al}_{2-y}\text{Mg}_y) \cdot \text{O}_{10}(\text{OH})_2$ ,  $x = 0.05\text{--}0.45$ ;  $y = 0.05\text{--}0.65$ . The montmorillonite group includes about 20 different minerals, among them the title mineral, montmorillonite, being the most abundant. The crystal structure of these minerals is characterized by layered arrangement of cations and anions (Fig. 1). Montmorillonite stacks have a plane of symmetry. They are faced to each other by similarly charged oxygen layers, thus stabilizing the aluminum(magnesium)–oxygen–hydroxo layers by the van der Waals forces.

Water and other polar liquids can easily penetrate into the interlayer space of the montmorillonite lattice, expanding the layers to the extent depending on the

amount of absorbed liquid. This structural feature promotes the use of montmorillonite as a filler for nanocomposites, since, to attain the required characteristics, a layered filler should be totally exfoliated in the polymer matrix.

At the same time, natural montmorillonite as a filler for polymer–inorganic nanocomposites demonstrates some drawbacks. For example, natural clay minerals represent mostly a mixture of several natural compounds, being, therefore, inhomogeneous in the chemical, phase, and disperse compositions. This makes the task of directed synthesis of functionalized nanocomposites more complicated.

To our best knowledge, in all the works on polymer–clay nanocomposites with montmorillonite as a filler, natural clay minerals were used, and the authors mostly gave no indication of their composition, rarely specifying the particle size. This does not allow establishment of the relationship between the composition and particle size of the filler and the properties of the resulting nanocomposite on the basis of published data. Establishment of such a relationship appears to be even more significant in view of the fact that no concept has been offered by now to explain the observed abrupt changes in characteristics of the polymers occurring with even small (2–3%) additions of montmorillonite.

Therefore, synthesis of montmorillonite of a fixed composition with a narrow particle size distribution is of considerable scientific and practical interest in view of its application as a filler in polymer–inorganic nanocomposites.

## EXPERIMENTAL

The goal of this work was hydrothermal synthesis of magnesium silicate montmorillonite  $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$  (analog of natural saponite) with a particle size of about 100 nm.

Optimization of the synthetic procedure was aimed at preparation of a single-phase product of a fixed composition with a narrow particle size distribution. Therefore, we studied the effects of such factors as the temperature, initial chemicals, reaction medium, and run duration on the yield and quality of the product.

As starting materials for the synthesis we used dry and ground silica gel  $SiO_2 \cdot nH_2O$ ,  $MgO$ , and  $Mg(OH)_2$  precipitated from a  $MgCl_2$  solution.

A stoichiometric mixture of the starting chemicals was treated with NaOH solutions of various concen-

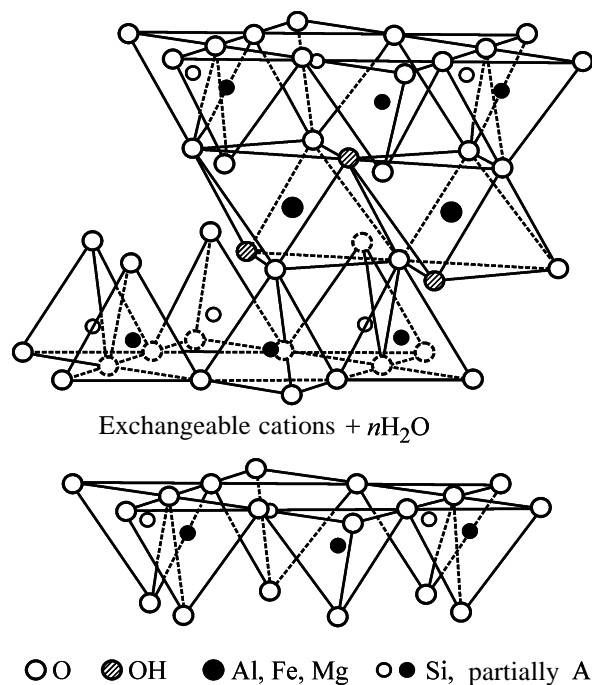


Fig. 1. Crystal structure of montmorillonite.

trations under hydrothermal conditions (250–350°C, 70 MPa) for 0.5–7 h.

The resulting products were examined by X-ray diffraction (DRON-3 diffractometer,  $CuK_{\alpha}$  radiation), crystal optics (MIN-8 microscope), and transmission electron microscopy (EM-125 electron microscope;  $U_{acc} = 75$  kV).

The synthesis conditions and characteristics of the resulting products are summarized in the table.

The results show that, in hydrothermal synthesis of montmorillonite, brucite  $Mg(OH)_2$  is the major impurity phase. Under certain conditions, the final product contains also other impurities such as magnesium oxide, quartz, and chrysotile (Fig. 2).

At 250 and 300°C, increasing alkalinity of the hydrothermal solution results initially in decrease in the montmorillonite content in the final product and increase in the brucite content (see table, experiment nos. 2, 3, and 7–9), and, with further increase, in a change montmorillonite/brucite ratio in the direction of increasing montmorillonite fraction (experiments nos. 4 and 5). In experiment no. 15 (350°C; 1 wt % NaOH), the product also contains  $MgO$ , which was not the case in experiment no. 14 performed with 3 wt % NaOH, all other conditions being equal.  $MgO$  was also found in the products obtained with 2.5 wt % NaOH at 250 and 300°C, but at a run time of 2 h (experiment nos. 1 and 6). Synthesis under the same

Synthesis conditions and characteristics of products ( $P = 70$  MPa)

Ex-periment no.	Starting chemicals		$T, ^\circ\text{C}$	$\tau, \text{h}$	Product	$I_{\text{MMT}}/I_{\text{br}}^*$	Particle size**
	solids	$c_{\text{NaOH}}$ , wt %, in hydrothermal solution					
1	MgO + SiO <sub>2</sub>	2.5	250	2	MMT + brucite + MgO		Coarse particles (up to 0.2–0.3 mm)
2	MgO + SiO <sub>2</sub>	2.5	250	4	MMT + brucite	1.2	
3	MgO + SiO <sub>2</sub>	3.0	250	4	MMT + brucite	0.7	
4	MgO + SiO <sub>2</sub>	3.5	250	4	MMT + brucite	0.75	
5	MgO + SiO <sub>2</sub>	4.0	250	4	MMT + brucite	1.1	
6	MgO + SiO <sub>2</sub>	2.5	300	2	MMT + brucite + MgO	–	
7	MgO + SiO <sub>2</sub>	2	300	4	MMT + brucite	1.7	
8	MgO + SiO <sub>2</sub>	2.5	300	4	MMT	–	
9	MgO + SiO <sub>2</sub>	4.0	300	4	MMT + brucite	0.8	Broad particle size distribution, the coarsest particles are up to 0.25 mm
10	MgO + SiO <sub>2</sub>	4.0	300	5	MMT + chrysotile + traces of brucite	–	
11	MgO + SiO <sub>2</sub>	3.0	300	7	MMT + brucite	1.9	Finely dispersed fraction dominates as separate particles and conglomerates (70–90%). Coarse plate-like particles are also present
12	MgO + SiO <sub>2</sub>	3.0	350	0.5	MMT + brucite + SiO <sub>2</sub>	–	
13	MgO + SiO <sub>2</sub>	3.0	350	0.75	MMT + brucite + SiO <sub>2</sub>	–	
14	MgO + SiO <sub>2</sub>	3.0	350	1	MMT + brucite	0.7	
15	MgO + SiO <sub>2</sub>	1.0	350	1	MMT + brucite + MgO	–	
16	MgO + SiO <sub>2</sub>	2.0	350	1	MMT + brucite	0.8	Broad particle size distribution, the coarsest particles are 0.2–0.3 mm in size
17	Mg(OH) <sub>2</sub> + SiO <sub>2</sub>	2.5	300	2	MMT + brucite	0.5	
18	Mg(OH) <sub>2</sub> + SiO <sub>2</sub>	3.0	300	1	MMT + brucite	0.7	

\* ( $I_{\text{MMT}}/I_{\text{br}}$ ) Montmorillonite (MMT) to brucite (br) ratio in the products. It was estimated from the X-ray diffraction data as the intensity ratio of the characteristic peaks of montmorillonite ( $2\theta = 60.5^\circ$ ,  $I_{\text{rel}} = 100\%$ ) and brucite ( $2\theta = 38^\circ$ ,  $I_{\text{rel}} = 100\%$ ).

\*\* Characteristics of as-prepared (not subjected to acid treatment) products, determined by the crystalloptical method.

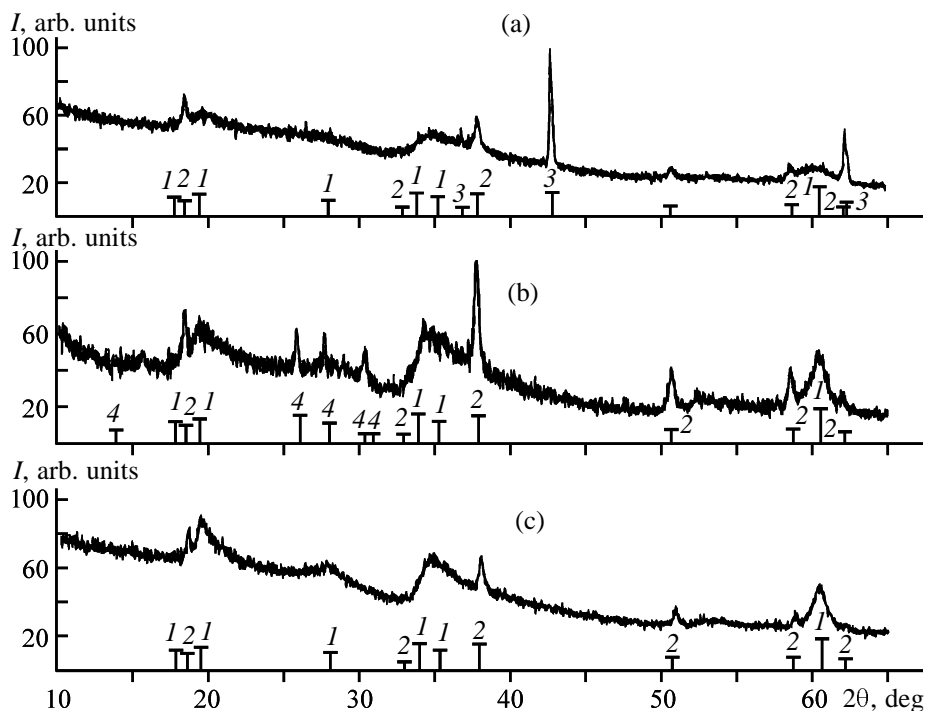
conditions, but for 4 h produces only montmorillonite and brucite (experiment nos. 2, 8). The use of more alkaline solutions (4 wt % NaOH) results in formation of brucite in considerable amount, and with increasing run time to 5 h, chrysotile is also formed (experiment no. 10).

According to the thermodynamic data (IVTAN-THERMO), magnesium hydroxide is stable over the experimental temperature and pressure ranges. Therefore, MgO that was found in the reaction products can be considered, most likely, as an unreacted initial component, but not as a decomposition product of brucite formed in the reaction.

It is known [11, 12] that the solubility of silica in a hydrothermal solution strongly increases in the presence of an alkali metal oxide, i.e., increase in the solution pH results in transfer of a considerable part of

SiO<sub>2</sub> into the liquid phase. Dissolution of silica in the system Na<sub>2</sub>O–SiO<sub>2</sub>–H<sub>2</sub>O may produce three phases: quartz, sodium silicate solution, and aqueous silicic acid. The latter two phases are liquids, and their compositions are temperature- and pressure-dependent [11]. Therefore, in performing the synthesis in alkaline solutions, the solid phase may be silica-deficient (relative to the fixed stoichiometry of montmorillonite). As a result, in addition to montmorillonite, other solid phases with a lower SiO<sub>2</sub> content can be formed, e. g., chrysotile (see table, experiment no. 10), and the final product will contain unreacted brucite.

According to the known classification of layered silicates [13] based on the layer structure, two major groups of minerals belong to the 1 : 1 and 2 : 1 types. In layered silicates of the 1 : 1 type, e.g., in chrysotile, a two-dimensional network built by SiO<sub>4</sub> tetrahedra is jointed to a two-dimensional network of MgO<sub>6</sub> octa-



**Fig. 2.** X-ray diffraction patterns of montmorillonite samples obtained under different synthetic conditions together with XRD data for reference compounds. (*I*) Intensity and ( $2\theta$ ) Bragg angle; the same for Figs. 3, 5, and 6. (a) 250°C, 2 h, 2.5% NaOH; (b) 350°C, 0.5 h, 3.0% NaOH; and (c) 300°C, 4 h, 3.5% NaOH. (1)  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , (2)  $\text{Mg}(\text{OH})_2$ , (3)  $\text{MgO}$ , and (4)  $\text{SiO}_2$ .

hedra. Montmorillonite is classed with layered silicates of the 2 : 1 type. In its structure, the octahedral layer is arranged between two tetrahedral layers (Fig. 1). Therefore, partial dissolution of silica may promote formation of chrysotile  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  whose structure contains smaller amount of  $\text{SiO}_2$  than in montmorillonite  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ .

Analysis of the effect of the alkalinity of the hydrothermal solution on crystallization of montmorillonite shows that increase in the NaOH concentration, first, increases the solubility of  $\text{SiO}_2$ , resulting in formation of chrysotile and brucite. At the same time, after formation of the nucleation centers, e.g., magnesium-oxygen octahedra in brucite, crystallization of montmorillonite is controlled by  $\text{SiO}_2$  transfer to the reaction zone. Therefore, increase in the NaOH concentration and the corresponding increase in the solubility of  $\text{SiO}_2$  in the hydrothermal solution should enhance the mass transfer of  $\text{SiO}_2$  and, therefore, the montmorillonite formation rate.

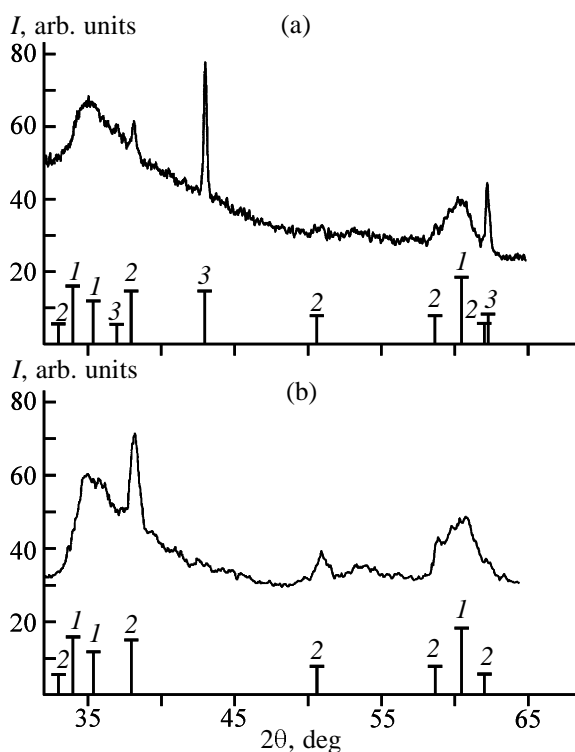
Furthermore, increasing alkalinity of the solution produces silicates with highly associated silicon-oxygen complex polyanions such as  $[\text{SiO}_3]^{2-}$  and  $[\text{Si}_2\text{O}_5]^{2-}$  [11]. Entering the reaction, these silicates promote formation of silicates with infinite silicon-

oxygen radicals, i.e., of layered silicates. This trend is supported by the data on the effect of the NaOH concentration in the hydrothermal solution: the yield of montmorillonite decreases on passing from 2.5 to 3.5 wt % NaOH (250°C; run time 4 h; see table, experiment nos. 2–4), and then increases as the NaOH concentration increases to 4 wt % (experiment no. 5; 4 wt % NaOH).

Finally, in low-alkaline solutions (1–2.5 wt % NaOH) and at small run time (2 h), the reaction between the starting components is incomplete. Increasing alkalinity to 3–4 wt % may result in stabilization of chrysotile. The maximal yield of montmorillonite was obtained at an alkalinity of 2–2.5 wt % NaOH at 350°C and run time of 2 h.

Increasing temperature from 250 to 300°C (4 h; experiment nos. 5 and 9) slightly increases the yield of montmorillonite and decreases the fraction of  $\text{Mg}(\text{OH})_2$  in the final product. Therefore, increasing temperature activates reactions between the initial components, promoting initially formation of brucite and then, of montmorillonite.

Similar trend was observed with respect to the run time. Increasing run time from 2 to 4 h at 250 and 300°C (2.5 wt % NaOH; experiment nos. 1, 2, 6,



**Fig. 3.** XRD patterns of montmorillonite samples synthesized using (a) MgO and (b) Mg(OH)<sub>2</sub> (experiment nos. 6 and 17).  $T = 300^{\circ}\text{C}$ ,  $\tau = 2$  h, and  $c_{\text{NaOH}} = 2.5$  wt %. (1) Montmorillonite  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , (2) Mg(OH)<sub>2</sub>, and (3) MgO.

and 8) increases the yield of montmorillonite and decreases the fraction of Mg(OH)<sub>2</sub> in the product with formation of single-phase montmorillonite (experiment no. 8;  $300^{\circ}\text{C}$ ; 2.5 wt % NaOH; 4 h).

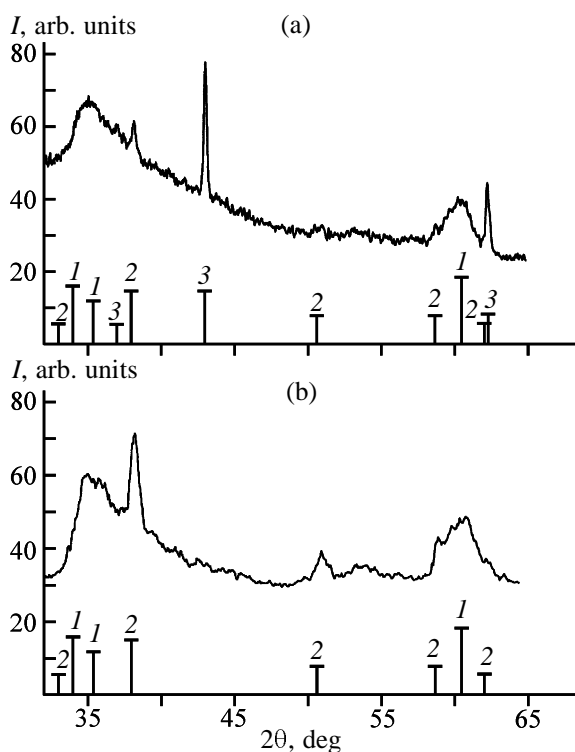
The following conclusions could be made on the formation mechanism of montmorillonite under hydrothermal conditions. In alkaline solutions, initial stages of the process involve hydration of MgO with formation of brucite and partial dissolution of SiO<sub>2</sub>. In the next stage, Mg(OH)<sub>2</sub> reacts with silica with formation of magnesium hydrosilicates, particularly, montmorillonite. Thus, the formation of Mg(OH)<sub>2</sub> precedes the formation of montmorillonite, which can be attributed to structural effects. Brucite has layered structure with the layers representing a magnesium–oxygen network [13]. Structurally these layers are similar to the magnesium–oxygen octahedral network arranged between the tetrahedral layers in the structure of montmorillonite. Evidently, Mg(OH)<sub>2</sub> plays a role of a nucleating center in crystallization of montmorillonite, which can be thought as formation of silicon–oxygen layers between still existing brucite layers through deposition of the silicon-containing component from the hydrothermal solution onto the layers of magnesium–oxygen octahedra.

Increasing run time, on the one hand, results in decreasing brucite fraction in the product, and, on the other hand, in increasing particle size.

Insofar as the goal of the work was synthesis of montmorillonite not of only the desired composition, but also with the optimal particle size distribution, we performed a series of experiments at higher temperature ( $350^{\circ}\text{C}$ ) and shorter run times (0.5–1 h) in hydrothermal solutions of various concentrations. Analysis of the resulting products revealed that synthesis in 3 wt % NaOH (experiment nos. 12, 13) affords products containing two impurity phases, Mg(OH)<sub>2</sub> and SiO<sub>2</sub>. According to the XRD data, the latter product represents a labile intermediate phase SiO<sub>2</sub>–X<sub>2</sub>. It is known [14, 15] that hydrothermal crystallization of amorphous silica into quartz is a complex process involving formation of a series of intermediate phases. Introduction of a sufficient amount of the alkali into the reaction medium causes formation of intermediate phases representing cation-filled polymorphs of silica (SiO<sub>2</sub>–X, kenyaite, SiO<sub>2</sub>–Y, and magadiite). Further hydrothermal treatment converts the intermediate crystalline phases to quartz.

When performing the synthesis in 2 wt % NaOH ( $350^{\circ}\text{C}$ ; 1 h), we obtained montmorillonite with the minimal content of Mg(OH)<sub>2</sub> and dominating finely disperse fraction (up to 90%). This result is well consistent with the above considerations on the effects of the NaOH concentration in the hydrothermal solution, temperature, and run time on the characteristics of the resulting montmorillonite.

As mentioned above, brucite serves as a nucleation center in crystallization of montmorillonite. Therefore, it appeared desirable to use Mg(OH)<sub>2</sub> instead of MgO as an initial component, to increase the yield of the final product and also to accelerate the process (experiment nos. 17 and 18). The crystalloptical data show that the samples prepared using Mg(OH)<sub>2</sub> contain relatively larger amount of the coarse fraction even at a shorter run time (1 h, experiment no. 18), which can be attributed to agglomeration of the initial Mg(OH)<sub>2</sub> particles. This conclusion is supported by the mean size of Mg(OH)<sub>2</sub> particles in the product, estimated from the XRD data by the Scherrer equation [16]. For the sample obtained in experiment no. 17 (2.5 wt % NaOH,  $300^{\circ}\text{C}$ , 2 h), the mean size of Mg(OH)<sub>2</sub> particles was estimated to be 46 nm. In conducting the reaction under the same conditions, but using MgO as a starting reagent (experiment no. 6), we obtained Mg(OH)<sub>2</sub> particles with a mean size of 90 nm, i.e., twice that obtained in the experiment with MgO. Figure 3 shows the XRD patterns of montmoril-



**Fig. 3.** XRD patterns of montmorillonite samples synthesized using (a) MgO and (b) Mg(OH)<sub>2</sub> (experiment nos. 6 and 17).  $T = 300^{\circ}\text{C}$ ,  $\tau = 2$  h, and  $c_{\text{NaOH}} = 2.5$  wt %. (1) Montmorillonite  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , (2) Mg(OH)<sub>2</sub>, and (3) MgO.

and 8) increases the yield of montmorillonite and decreases the fraction of Mg(OH)<sub>2</sub> in the product with formation of single-phase montmorillonite (experiment no. 8;  $300^{\circ}\text{C}$ ; 2.5 wt % NaOH; 4 h).

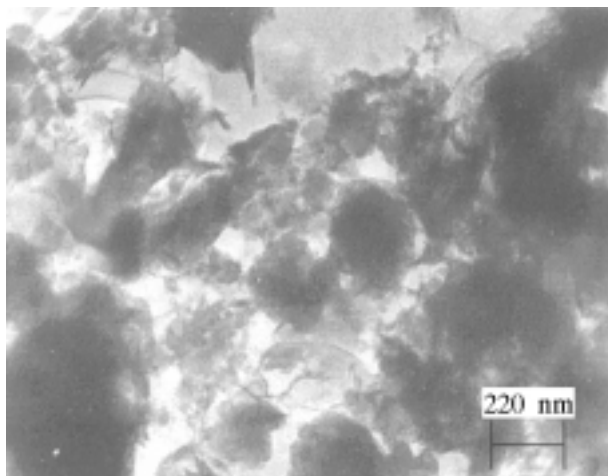
The following conclusions could be made on the formation mechanism of montmorillonite under hydrothermal conditions. In alkaline solutions, initial stages of the process involve hydration of MgO with formation of brucite and partial dissolution of SiO<sub>2</sub>. In the next stage, Mg(OH)<sub>2</sub> reacts with silica with formation of magnesium hydrosilicates, particularly, montmorillonite. Thus, the formation of Mg(OH)<sub>2</sub> precedes the formation of montmorillonite, which can be attributed to structural effects. Brucite has layered structure with the layers representing a magnesium–oxygen network [13]. Structurally these layers are similar to the magnesium–oxygen octahedral network arranged between the tetrahedral layers in the structure of montmorillonite. Evidently, Mg(OH)<sub>2</sub> plays a role of a nucleating center in crystallization of montmorillonite, which can be thought as formation of silicon–oxygen layers between still existing brucite layers through deposition of the silicon-containing component from the hydrothermal solution onto the layers of magnesium–oxygen octahedra.

Increasing run time, on the one hand, results in decreasing brucite fraction in the product, and, on the other hand, in increasing particle size.

Insofar as the goal of the work was synthesis of montmorillonite not of only the desired composition, but also with the optimal particle size distribution, we performed a series of experiments at higher temperature ( $350^{\circ}\text{C}$ ) and shorter run times (0.5–1 h) in hydrothermal solutions of various concentrations. Analysis of the resulting products revealed that synthesis in 3 wt % NaOH (experiment nos. 12, 13) affords products containing two impurity phases, Mg(OH)<sub>2</sub> and SiO<sub>2</sub>. According to the XRD data, the latter product represents a labile intermediate phase SiO<sub>2</sub>–X<sub>2</sub>. It is known [14, 15] that hydrothermal crystallization of amorphous silica into quartz is a complex process involving formation of a series of intermediate phases. Introduction of a sufficient amount of the alkali into the reaction medium causes formation of intermediate phases representing cation-filled polymorphs of silica (SiO<sub>2</sub>–X, kenyaite, SiO<sub>2</sub>–Y, and magadiite). Further hydrothermal treatment converts the intermediate crystalline phases to quartz.

When performing the synthesis in 2 wt % NaOH ( $350^{\circ}\text{C}$ ; 1 h), we obtained montmorillonite with the minimal content of Mg(OH)<sub>2</sub> and dominating finely disperse fraction (up to 90%). This result is well consistent with the above considerations on the effects of the NaOH concentration in the hydrothermal solution, temperature, and run time on the characteristics of the resulting montmorillonite.

As mentioned above, brucite serves as a nucleation center in crystallization of montmorillonite. Therefore, it appeared desirable to use Mg(OH)<sub>2</sub> instead of MgO as an initial component, to increase the yield of the final product and also to accelerate the process (experiment nos. 17 and 18). The crystalloptical data show that the samples prepared using Mg(OH)<sub>2</sub> contain relatively larger amount of the coarse fraction even at a shorter run time (1 h, experiment no. 18), which can be attributed to agglomeration of the initial Mg(OH)<sub>2</sub> particles. This conclusion is supported by the mean size of Mg(OH)<sub>2</sub> particles in the product, estimated from the XRD data by the Scherrer equation [16]. For the sample obtained in experiment no. 17 (2.5 wt % NaOH,  $300^{\circ}\text{C}$ , 2 h), the mean size of Mg(OH)<sub>2</sub> particles was estimated to be 46 nm. In conducting the reaction under the same conditions, but using MgO as a starting reagent (experiment no. 6), we obtained Mg(OH)<sub>2</sub> particles with a mean size of 90 nm, i.e., twice that obtained in the experiment with MgO. Figure 3 shows the XRD patterns of montmoril-



**Fig. 4.** Electron micrograph of montmorillonite prepared by hydrothermal synthesis.

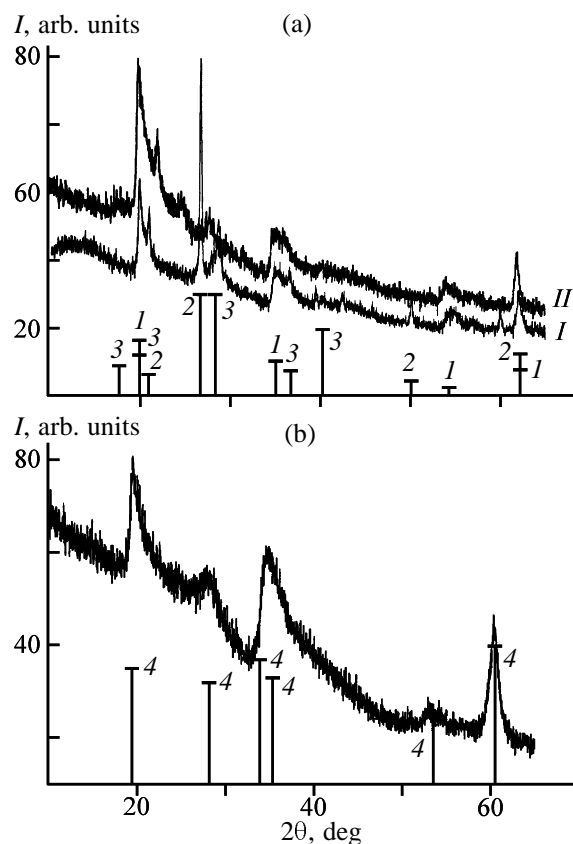
lonite samples obtained from  $\text{MgO}$  and  $\text{Mg}(\text{OH})_2$ .

To obtain single-phase finely dispersed montmorillonite, the samples were treated with 1 M HCl. Such a treatment allows removal of impurity phases, if they formed. At the same time, it is known [17] that acid treatment decreases the mechanical strength of clays through weakening the interparticle interactions and also interlayer interactions in the structure of clay minerals, realized with participation of the adsorbed water molecules. Such a disaggregation of the particles favors their dispersion in the polymer matrix in preparation of nanocomposites.

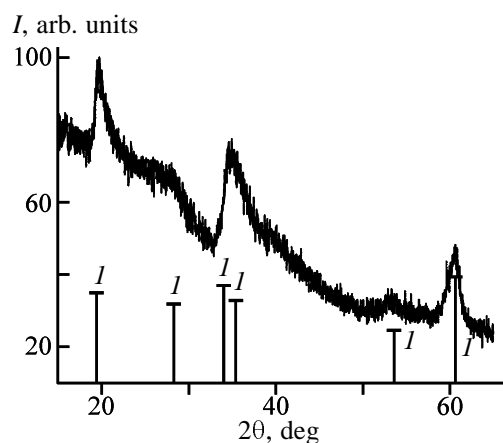
Using acid treatment of montmorillonite samples prepared under different conditions, we obtained single-phase samples of magnesium silicate montmorillonite with a particle size of 50–100 nm (Fig. 4).

As mentioned above, the authors of studies devoted to preparation and characterization of polymer–inorganic nanocomposites used either natural montmorillonite or modified clay materials [2–10]. In both cases, the starting materials represented mixtures of several natural compounds.

Figures 5 and 6 show XRD patterns of natural montmorillonite, of MMT- $\text{Na}^+$  modified montmorillonite (Southern Clay Products, Inc.), which is most often used in preparation of nanocomposites [4, 5], and also of the samples synthesized in this work (Figs. 5b, 6). Comparison of the XRD patterns (Figs. 5, 6) reveals that synthetic montmorillonite differs advantageously from its natural analogs in that it contains no impurity phases. Furthermore, it follows from electron microscopic data that the particles of



**Fig. 5.** XRD patterns: (a) (I) natural montmorillonite and (II) modified montmorillonite MMT- $\text{Na}^+$ ; (b) synthetic montmorillonite (see table, experiment no. 8). (1) Montmorillonite  $\text{Na}_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , (2)  $\text{SiO}_2$  (quartz), (3) rectorite  $\text{K}_{1.2}\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ , and (4) montmorillonite  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ .



**Fig. 6.** XRD pattern of synthetic montmorillonite (experiment no. 12) after acid treatment. (1)  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ .

synthetic montmorillonite are from 50 to 100 nm in size, whereas natural montmorillonite is characterized by broader particle size distribution (from 50 to 250 nm and more) (Figs. 4, 7).