

PHYSICO-CHEMICAL FEATURES OF THE SYNTHESIS OF MULLITE IN MIXTURES OF QUARTZ-PYROPHYLLITE ROCK WITH A FLUORIDE-FORMING COMPONENT

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It is established that the use of an ammonium fluoride treatment on quartz-pyrophyllite rock (45% pyrophyllite and 53% quartz) at 650°C changes the traditional mechanism by which mullite is synthesized; it is formed not from metapyrophyllite but from fluoridated pyrophyllite, with the formation of aluminum trifluoride and topaz being intermediate stages of the synthesis process. The optimum ratio of quartz-pyrophyllite rock to ammonium hydrodifluoride is 1:1.6, which at 1300°C increases the yield of acicular mullite (with particles 20 – 30 μm long and 3 – 5 μm in cross section) from 12 to 68 wt.%. The content of residual quartz in the mullite is no greater than 15 – 18 wt.%.

Keywords: pyrophyllite, ammonium hydrodifluoride, fluoridation, heat treatment, synthesis, phase formation, mullite, topaz, corundum.

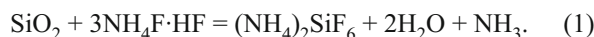
Alumosilicate ceramics with a crystalline mullite phase have now come into wide use in different areas of science and industry. The excellent functional properties of these ceramics are determined not only by the total content of mullite but also by its structural-morphological state (prismatic particles or acicular particles).

The main problem encountered in attempting to obtain mullite from the natural alumosilicate raw material is that efficient new low-temperature methods need to be found to synthesize mullite in order to produce mullite ceramics in which the content of the glassy phase is low and the mullite has a non-isometric habit. Together, these characteristics improve the service properties of the ceramic: chemical stability, heat resistance, refractoriness, and mechanical strength at room temperature and high temperatures.

One method that is used on an industrial scale to obtain alumosilicate ceramics from natural raw materials and maximize the yield of mullite entails the addition of an alumina-bearing component so that the silica which is formed during thermal degradation of the rock-like minerals (pyrophyllite, kaolinite, etc.) is bound inside the secondary mullite of the material. Another approach which might hold promise as a means of increasing the amount of mullite that is formed

is to enrich the product obtained from firing the natural alumosilicate raw material by having the silica component separated out during the process of synthesizing mullite. The silica component can be obtained either in the form of the free quartz which is always present in the raw material or as a structural component of the alumosilicate mineral.

In connection with this, it is interesting to examine the use of a method which uses fluorine ions to decompose silicates [1 – 3]. The fluoride-forming agents that are the most convenient to use to break down silicate materials are fluorides of ammonia. Under normal conditions, these fluorides are nonaggressive crystalline substances which when heated react with silica as follows to form ammonium hexafluorosilicate:



The ability of the ammonium hexafluorosilicate which is formed to undergo sublimation at 320° makes it possible to effectively remove it (and thus eliminate excess silica) from the alumosilicate matrix, which in turn makes it possible to increase the yield of mullite. In the investigation being discussed in this article, the natural alumosilicate raw material which was used was pyrophyllite-bearing rock from the Kul-Yurt-Tau deposit (in the Republic of Bashkortostan).

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Fig. 1. Electron micrograph of pyrophyllite rock. $\times 5000$.

The structural-phase changes that take place in pyrophyllite when it is heated have been described in satisfactory detail in the specialized literature [4–6], although the data that has been presented on the temperature ranges within which the phases that are formed exist is somewhat contradictory. What is agreed upon as fact is that the products from the dissociation of pyrophyllite are mullite and silica — the

formation of which adversely affects the properties of aluminosilicate ceramics based on pyrophyllite.

Studies were made of the physico-chemical and processing properties of pyrophyllite rock from the Kul-Yurt-Tau deposit. The results showed that in terms of its chemical composition (Table 1) the rock can (in accordance with the classification of clay-based materials) be regarded as an acidic aluminosilicate raw material based on its content of Al_2O_3 in the calcined state (less than 15%). The rock also has a low content of coloring oxides (the combined content of Fe_2O_3 and TiO_2 in the calcined state is less than 0.5 wt.%).

In terms of its mineralogical composition, the pyrophyllite rock is a quartz-pyrophyllite facies containing more quartz (53.3 wt.%) than pyrophyllite (45.5 wt.%). The rock-forming mineral component (pyrophyllite) is in the aggregated state and consists mainly of the 0.25–0.063 mm fraction. This confirms reports that pyrophyllite is encountered in nature in the form of actinic lamellar deposits. In addition to the 0.25–0.06 mm fraction, the quartz component of the rock consists of coarse fractions with particles sizes ranging from 1 to 0.25 mm.

The use of mi8 electron microscopy showed that the rock is comprised of lamellar isometric particles ranging in size from 2 to 10 μm (Fig. 1).

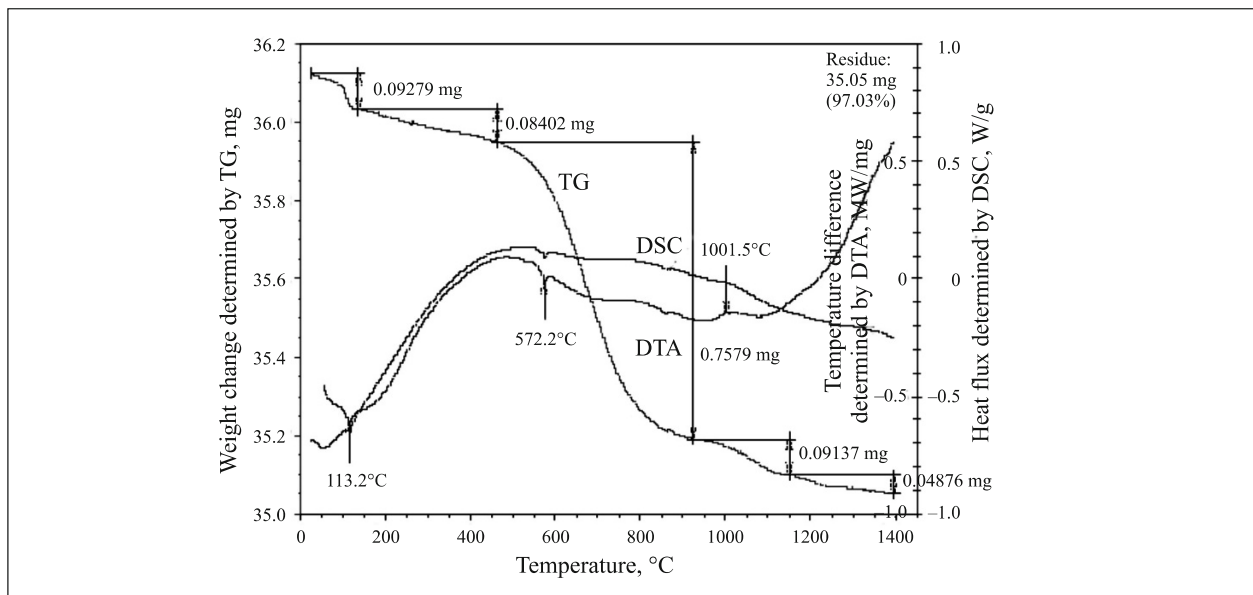


Fig. 2. Curves from thermal analysis of pyrophyllite rock from the Kul-Yurt-Tau deposit.

TABLE 1. Chemical Composition of Pyrophyllite Rock from the Kul-Yurt-Tau Deposit

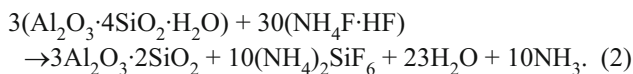
State	Content of oxides, %									$\Delta m_{\text{cal}}, \%$
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	
Air-dried	83.76	12.85	0.13	0.33	0.08	0.12	0.17	Ñě.	0.16	2.40
Calcined	85.82	13.17	0.13	0.34	0.08	0.12	0.17	Ñě.	0.16	—

Analysis of the pyrophyllite rock by differential-scanning calorimetry (DSC) (Fig. 2) showed that its dehydration takes place in several stages. In particular, chemically bound water begins to be removed from the structure of the pyrophyllite at 450–460°C due to the loss of water by the finer and more defective particles of the mineral. Dehydration of most of the pyrophyllite occurs within the temperature range from 500 to 800°C. Pyrophyllite undergoes dehydration over a much broader temperature range than kaolinite and other natural aluminosilicates due to the more rigid bonds between the $[\text{SiO}_4]$ and $[\text{Al}(\text{O},\text{OH})_6]$ groups in the mineral's structure. The difference in the bonds creates differences between the relative importance of the positions of the (OH) groups in relation to the aluminum atoms. The presence of the endothermic effect on the DTA curve of pyrophyllite rock at 572°C is attributable to the polymorphism of the quartz component, and, as already noted, the content of this component in the rock is substantial.

X-ray diffraction and infrared spectroscopy were used to study phase-formation processes during the heating of pyrophyllite rock in the range 600–1300°C. The results showed that during heating of the rock the main crystalline phase (mullite) begins to form at 1200°C. By the time 1300°C is reached, the amount of mullite present is just 12.3% of the amount that is theoretically possible. Synthesis of the mullite takes place via the formation of an intermediate phase in the form of metapyrophyllite at 650°C. In the temperature range 1000–1300°C, only part of the quartz component in the original rock is still in the form of residual quartz. Most of it has already been converted to metastable cristobalite and undergone the associated changes in volume.

Thus, the large amount of free quartz (54 wt.%) in the pyrophyllite rock of the Kul-Yurt-Tau deposit limits the potential for using this rock in its original state to obtain high-quality aluminosilicate ceramics and makes it necessary to increase the rock's content of pyrophyllite. One way this could be done is by removing silica during ammonium fluoride treatment.

The process of obtaining mullite from pyrophyllite with the use of ammonium hydrodifluoride (AHDF) as the fluoride-forming agent can be represented by the following formula for the gross chemical reaction which takes place:



To evaluate the possibility of a low-temperature reaction between pyrophyllite and ammonium hydrodifluoride and explore the nature of the reaction, we examined the physico-chemical processes that take place in mixtures of pyrophyllite rock (Table 2) with a deficit of AHDF (compositions *P1* and *P2*) and with the amount of AHDF that was stoichiometrically correct with respect to mullite (composition *P3*).

Derivatographic studies of the mixtures of pyrophyllite rock and AHDF showed that the presence of ammonium

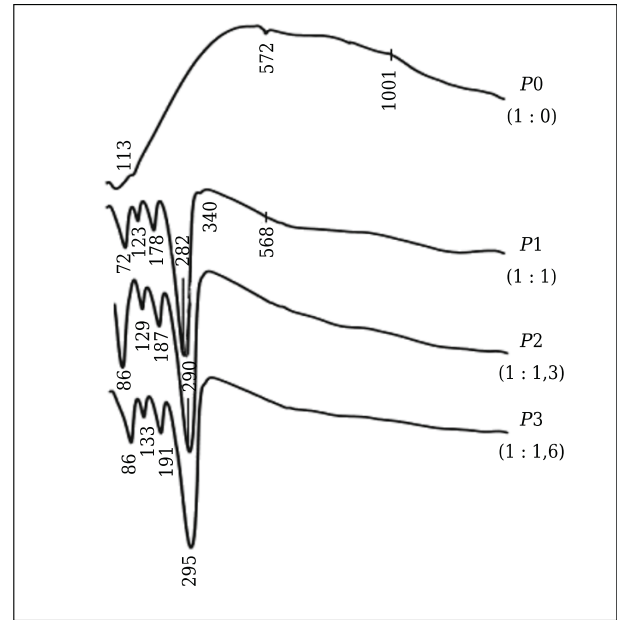


Fig. 3. DTA curves of mixtures of pyrophyllite rock and AHDF in relation to the ratio of these components. The temperature in degrees Celsius (°C) is shown next to the curves.

hydrodifluoride in the charge affects the behavior of the pyrophyllite during heating; it alters the temperature range within which the mineral undergoes dehydration and its crystalline lattice disintegrates.

In particular, in contrast to the original pyrophyllite rock (*P0*), the DTA curves of the rock's mixtures with AHDF (Fig. 3) include intense endothermic effects that reflect the reactions of the components of the pyrophyllite rock with AHDF.

The first endothermic effect, at 72–86°C, is related to the reaction of AHDF with physically bound water and the accompanying formation of ammonia. The next two endothermic effects, with minima at 123–133 and 178–191°C, are due to melting and evaporation of excess or unreacted AHDF, respectively. The endothermic effect seen on the DTA curves at 282–295°C is due to sublimation of the ammonium hexafluorosilicate which is formed in the reaction of

TABLE 2. Component-by-Component Composition of Mixtures of Pyrophyllite Rock with AHDF

Composition	Pyrophyllite:AHDF ratio	Content of components in the mixture, wt.%	
		pyrophyllite rock	AHDF
<i>P0</i>	1 : 0 — without fluoride	100	0
<i>P1</i>	1 : 1 } with deficit of fluoride	50.00	50.00
<i>P2</i>		43.48	56.52
<i>P3</i>	1 : 1.6 — stoichiometric ratio	38.46	61.54

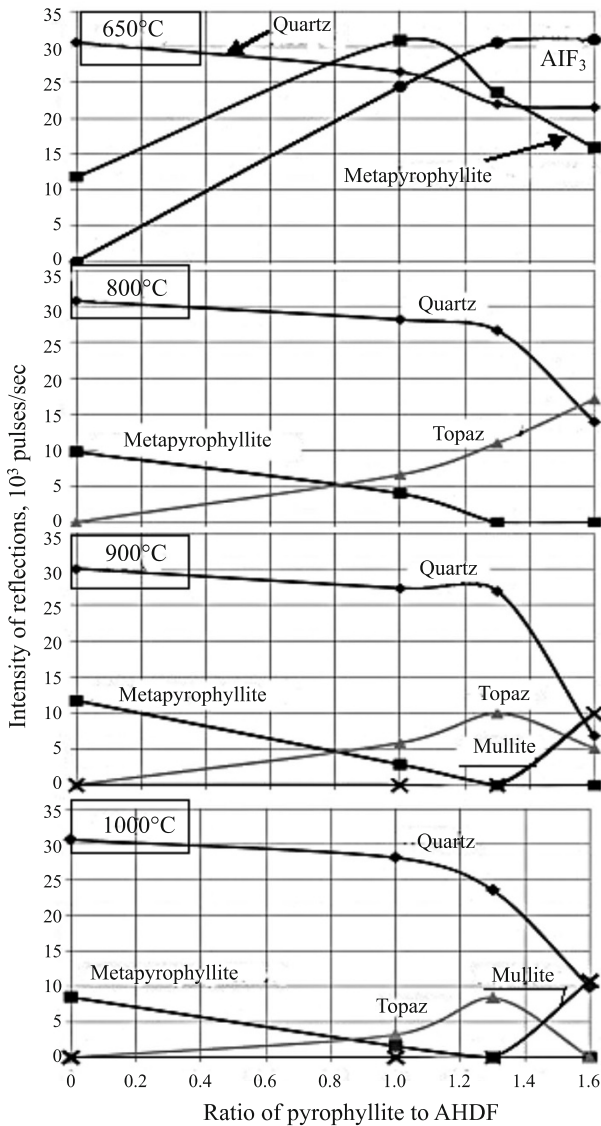


Fig. 4. Change in the intensity of the x-ray reflections of crystalline phases in low-temperature-fired (800–1000°C) specimens obtained from mixtures of pyrophyllite rock and AHDF fluoridated at 650°C.

AHDF with silica. This is readily seen on the TG curves, which show total weight losses of up to 70–75%.

The ammonium-fluoride treatment of pyrophyllite rock was carried out by heating mixtures of finely ground rock and a suitable weighed portion of ammonium hydrodifluoride at 650°C for 1 h. The fluoridation temperature was chosen based on the need to completely remove the ammonium hexafluorosilicate formed by the products of fluoridation of the pyrophyllite rock in reaction (1). Then specimens of the thermally fluoridated mixtures were heated within the range 800–1300°C.

Comparison of the derivatographic results and the data obtained from x-ray diffraction and IR spectroscopy confirmed that the presence of ammonium hydrodifluoride not

only alters the process of the thermal degradation of pyrophyllite but also fundamentally changes the way in which mullite is synthesized from pyrophyllite.

In particular, it was found that the process of the synthesis of mullite in the product obtained from the fluoridation of pyrophyllite passes through a stage in which aluminum trifluoride and topaz are formed as intermediate products. The exact compositions and quantities of the intermediate products formed by the thermal fluoridation of pyrophyllite rock depend on the amount of fluoride-forming agent that is introduced (Fig. 4). It was established that aluminum trifluoride and metapyrophyllite mixed with residual (unreacted) quartz were the products formed (Fig. 4) from the fluoridation of the mineral components of quartz-pyrophyllite rock at 650°C, regardless of whether the test mixtures had a deficit of AHDF (compositions *P1* and *P2*, with a rock:AHDF ratio equal to 1:1 and 1:1.3, respectively) or were stoichiometric (composition *P3*, for which the pyrophyllite:AHDF ratio = 1:1.6). The fact that the intensity of the quartz reflections in the fluoridated product was lower than for the original pyrophyllite rock heat-treated at 650°C without AHDF indicates that the AHDF reacted extensively with the coarse quartz component of the quartz-pyrophyllite rock and formed ammonium hexafluorosilicate by means of reaction (1).

Calcining of the products of fluoridation of mixture *P1* at temperatures from 800 to 1000°C resulted in the appearance of reflections of a new phase — topaz. The reflections of metapyrophyllite were still present in this case. These results show that the indicated concentration of AHDF in the *P1* mixture with quartz-pyrophyllite rock (pyrophyllite:AHDF = 1:1) is insufficient to completely break up the pyrophyllite lattice under the given conditions of the process (fluoridation at 650°C and subsequent calcining at 800–1000°C).

In mixture *P2* (pyrophyllite:AHDF = 1:1.3), the higher concentration of AHDF results in more active destruction of the pyrophyllite lattice during fluoridation, and calcination of the fluoridated mixture at 800°C leaves only topaz and quartz as the products. Metapyrophyllite is completely absent. Topaz and quartz are also the products when the calcination operation is carried out at temperatures up to 1000°C.

To judge from the intensity of the x-ray reflections, calcination of fluoridated mixture *P3* at 800°C reduced the content of residual quartz by almost half compared to the original rock and resulted in the synthesis of a substantial quantity of topaz. All of the metapyrophyllite decomposed. The metapyrophyllite in the original (non-fluoridated) rock remained present up to 1100°C.

Results obtained from scanning electron microscopy (Fig. 5) showed that the particles which were formed (topaz, according to our data) had an elongated prismatic form. The crystals were up to 10 μm in length.

An increase in the temperature used to calcine fluoridated mixture *P3* to 900°C resulted in a nearly threefold reduction in quartz content, partial decomposition of the topaz, and the formation of mullite. These results can be attributed

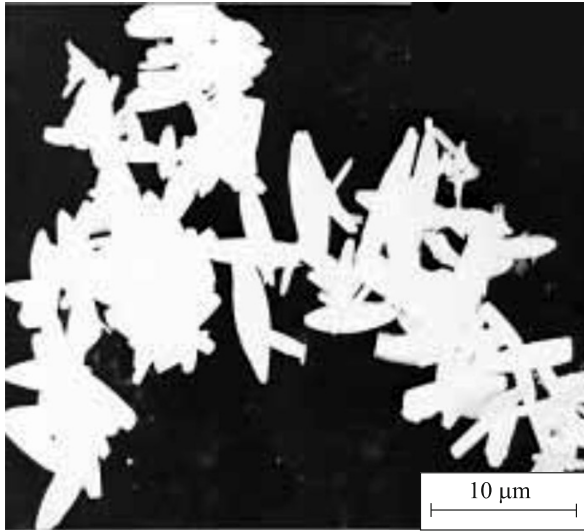


Fig. 5. Electron micrographs of mixture *P3* fluoridated at 650°C and calcined at 800°C. $\times 3000$.

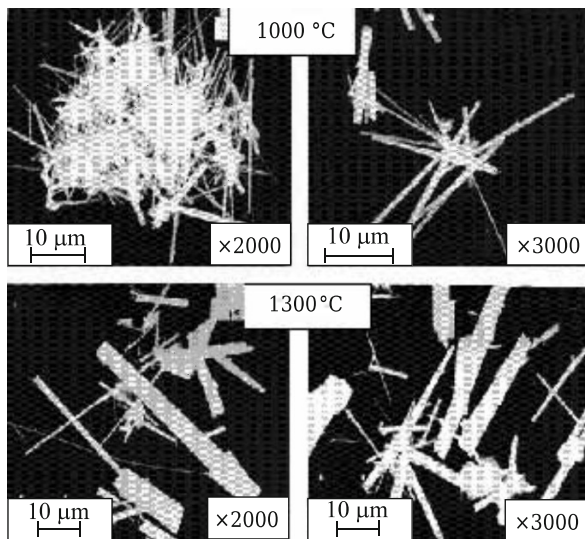


Fig. 6. Electron micrographs of mixture *P3* fluoridated at 650°C and calcined at 1000 and 1300°C.

to the fact that the amount of AHDF which was used in this case was sufficient to ensure complete destruction of the crystalline lattice of pyrophyllite and at relatively low temperatures (900°C) enable the formation of a mullite structure from the pyrophyllite (via the topaz-forming stage). In the non-fluoridated pyrophyllite, the presence of mullite begins to be detected roentgenographically (in trace amounts) only beginning at 1200°C.

An increase in the heating temperature from 900 to 1000°C did not significantly change the diffraction pattern of stoichiometric fluoridated mixture *P3*. The intensity of the mullite reflections increased and the topaz reflections completely disappeared, while the reflections of residual quartz

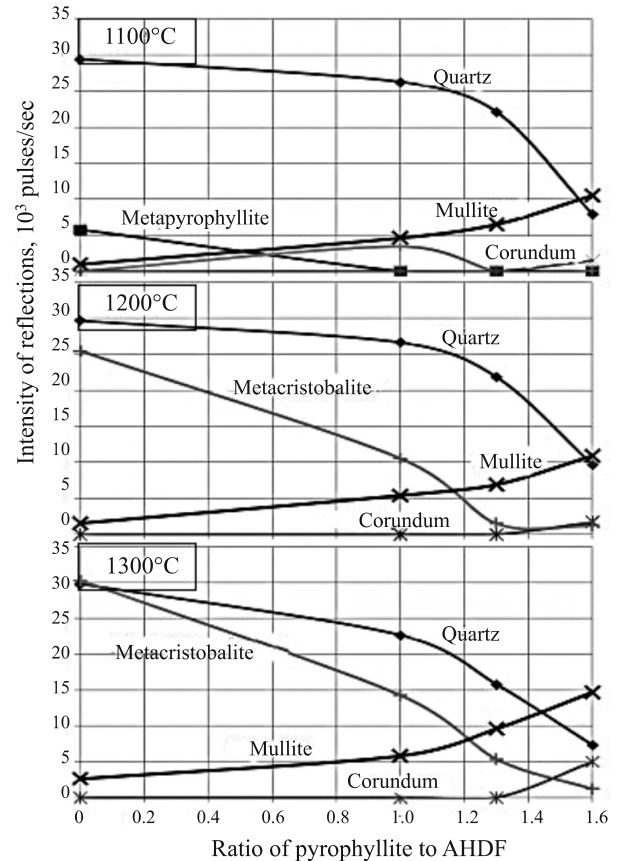


Fig. 7. Change in the intensity of the x-ray reflections of crystalline phases in high-temperature-fired (1100 – 1300°C) specimens obtained from mixtures of pyrophyllite rock and AHDF fluoridated at 650°C.

remained present. The mullite that was formed had a pronounced acicular structure (Fig. 6) with needles 10 – 20 μm in size. Intermingling with one another, the needles formed crystalline concretions that strengthened the structure of the material. This phenomenon can help obtain high-strength refractory materials in the future.

A further increase in the temperature at which fluoridated mixture *P3* was calcined to 1300°C led to the appearance of mullite as the main phase. A certain amount of quartz remained present, there were traces of cristobalite, and a certain amount of corundum was formed (Fig. 7). The mullite needles increased to 20 – 30 μm in length and 3 – 5 μm in diameter (Fig. 6).

As regards AHDF-deficient mixtures *P2* and *P3*, relatively low-intensity mullite reflections appeared on the diffraction patterns only after calcining at 1100°C. The intense quartz reflections were still present in the patterns in this case (Fig. 7).

An increase in calcining temperature to 1200 – 1300°C for all of the fluoridated mixtures led to the appearance of cristobalite in metastable form as a new reaction product. The fact that the intensity of the reflections of the silica com-

ponent of the mixtures (both in the form of residual quartz and in the form of metacristobalite) decreased - the size of the decrease depending on the increase made in the mixtures' content of the fluoride-forming agent - shows that silica was actively being removed from the quartz-pyrophyllite rock under the given conditions.

CONCLUSION

Thus, the above-described investigation established that ammonium-fluoride treatment of quartz-pyrophyllite rock at 650°C changes the traditional mechanism by which mullite is synthesized from pyrophyllite. Instead of there being an intermediate stage that entails the formation of metapyrophyllite, mullite is synthesized from fluoridated pyrophyllite via a stage in which aluminum trifluoride and topaz are formed as intermediate products.

It was found that fluoridation of quartz-pyrophyllite rock lowers the temperature at which the structure of pyrophyllite (metapyrophyllite) undergoes complete dissociation from 1100 to 800°C and lowers the temperature at which acicular mullite is synthesized from 1200 to 900°C. The optimum ratio of quartz-pyrophyllite rock to ammonium hydrodifluoride is 1:1.6. At 1300°C, this ratio increases the yield of acicular mullite (with particles 20 – 30 μm in length and 3 – 5 μm in

diameter) from 12 to 68 wt.%. Becoming intertwined with one another, the needles form a reinforcing crystalline concretion that can help produce high-strength ceramics in the future.

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