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Possibilities of Exchange Mechanochemical Reactions in the Synthesis of Magnesium Silicates

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Abstract

Nanodispersed powders of magnesium meta- and orthosilicates were obtained with the help of the solid-phase exchange reaction of magnesium chloride with sodium silicate using or not using NaOH. The reaction proceeds during mechanical activation. The formation of enstatite and forsterite occurs through the amorphous (or weakly crystallized) hydrated compound during subsequent thermal treatment. A comparison with the known method of obtaining these silicates through mechanical activation of the mixtures of magnesium hydroxide with silica gel is carried out.

Key words: magnesium silicates, mechanochemical synthesis, exchange reactions, hydrated salts and oxides, dispersed powder

INTRODUCTION

Mechanochemical synthesis of oxides and oxide materials can be performed through the mechanical activation of the mixtures of solid reagents in high-energy grinding devices and at present it is widely used to obtain solid compounds in the ultrafine state. As the development of this method, the authors of [1] proposed its version termed “soft mechanochemical synthesis”, when the mixtures of solid compounds containing hydroxyl groups and bound water (hydroxides and acids, basic and acidic salts, crystal hydrates *etc.*) undergo mechanical activation. The hardness of these compounds is lower than that of anhydrous compounds, which allows one to decrease the level of mechanical load during activation. Investigation of the processes occurring during this synthesis is very important for solid state chemistry.

The MgO–SiO₂ system was several times considered from the viewpoint of the possible mechanochemical synthesis of magnesium silicates – enstatite (MgSiO₃) and forsterite (Mg₂SiO₄). In the studies of the mixture of magnesium hydroxide with silica gel which is usually activated, the acid-base character of the solid-phase reaction is stressed (the reaction proceeds with the formation of the new

amorphous phase or Si–O–Mg bond [2, 3]. A detailed investigation of the products of synthesis and thermal treatment of the mixture of magnesium oxide or hydroxide with silicon dioxide hydrated to different extents, with Mg/Si = 1, was described in [4]. After long-term activation of the mixture (480–1200 rpm), the formation of the crystal phase was detected; it was the layered magnesium silicate which was composed, in the opinion of authors, of a mixture of talc- and chrysotyl-like products. A similar product is also formed under hydrothermal conditions, so the assumption concerning the hydrothermal mechanism of this process was put forward.

The goal of the present work was to investigate the formation of magnesium silicates and to reveal the nature of intermediate states during solid-phase reactions between the reagents of different nature.

EXPERIMENTAL

Mechanical activation for 10–100 min was performed using the planetary mill EI-2-150 (acceleration: 40g) with titanium cylinder and the balls made of titanium carbonitride, 8 mm in diameter. The compositions of the mixtures under treatment are listed in Table 1. After acti-

vation, some samples were washed to remove sodium chloride, and dried at room temperature. All the samples were subjected to thermal treatment in the air at 150–1200 °C with exposure for 2–4 h at each selected temperature point.

X-ray studies of powder samples were carried out with a DRON-3 diffractometer ($\text{CuK}\alpha$ radiation). The samples were recorded within the range $2\theta = 7\text{--}90^\circ$ at a rate of $0.5^\circ\text{C}/\text{min}$. Lattice parameters a , b , c , the sizes of crystallites (d), lattice microdeformations $\Delta\alpha/\alpha$ were calculated using Powder Cell 2.4 software. The infrared absorption spectra of samples in KBr tablets were recorded with a Specord M40 spectrometer. Thermal analysis was performed with a Netzsch STA 449C Jupiter in the air medium.

RESULTS AND DISCUSSION

Treatment in the activator at room temperature for 10 min of the mixture of magnesium chloride and sodium metasilicate ($\text{Mg}/\text{Si} = 1$) is accompanied by the formation of well crystallized sodium chloride and an X-ray amorphous product. The appearance of the reflections of NaCl in the X-ray diffraction patterns ($2\theta = 27.5, 31.8, 45.7, 56.5^\circ$) points to the fact that the activation of this mixture involves solid-phase exchange reaction between the initial components. Thermograms of the activated

sample exhibit two endothermic effects in the region of 130 and 805 °C; the former effect is caused by the removal of weakly bound water, while the latter one is due to NaCl melting (Fig. 1). It also follows from the analysis of the DTA data that the whole magnesium is present in the reaction products in the bound state because the endothermic effect in the region of 410 °C, which is characteristic of the dehydration of $\text{Mg}(\text{OH})_2$, is absent in this case. This is also confirmed by the data of IR absorption spectra: no band in the region of 3690 cm^{-1} corresponding to the stretching vibrations of hydroxide groups in magnesium hydroxide is observed. At the same time, the comparative analysis of the IR absorption spectra of activated samples (bands at 460, 620–680, 900 and 1020 cm^{-1}) and the samples of hydrated silicon dioxide $\text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$ (bands at 460, 580, 800, 930, 1090 cm^{-1}) shows that free (unbound) silicon dioxide is also absent from the formed reaction products (Fig. 2). So, X-ray amorphous product that is formed along with NaCl in the activated sample is likely to be hydrated magnesium silicate of the type $\text{MgO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$. One can see from the data shown in Fig. 2 that this compound remains almost unchanged during washing and subsequent thermal treatment up to 500 °C inclusive. Sodium chloride formed

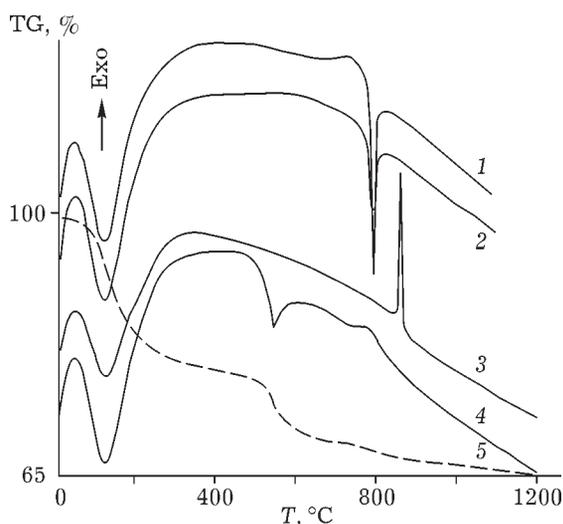


Fig. 1. DTA (1–4) and TG (5) curves of the samples of mixture $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1, 3) and $2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}) + \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} + 2\text{NaOH}$ (2, 4, 5) after mechanical activation (1, 2) and further washed to remove NaCl (3–5).

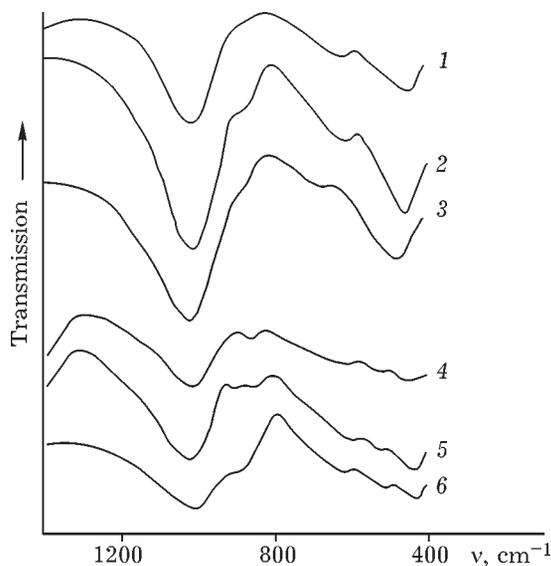


Fig. 2. IR spectra of the samples obtained by the activation of the mixture of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (1–3) and $2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}) + \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} + 2\text{NaOH}$ (4–6): 1, 4 – mechanically treated for 10 min; 2, 5 – washed to remove NaCl; 3, 6 – annealed at 500 °C.

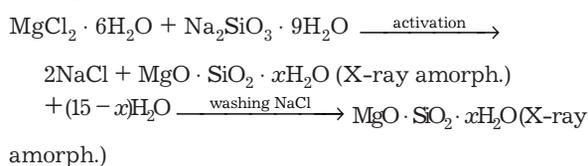
TABLE 1

Composition of reaction mixture and characterization of the samples obtained using mechanochemical method

Reaction mixture	τ , min	T , °C	Phase composition	d , nm	$\Delta\alpha/\alpha$, %	Lattice parameter, nm		
						a	b	c
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	10	900	MgSiO_3	15	0.14	0.921	0.884	0.523
		1200	MgSiO_3	31	0.05	0.925	0.883	0.533
$2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}) + \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} + 2\text{NaOH}$	10	900	Mg_2SiO_4	25	0.40	1.019	0.597	0.475
		1200	Mg_2SiO_4	41	0.05	1.020	0.598	0.475
$\text{Mg}(\text{OH})_2 + \text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$	10	900	Mg_2SiO_4					
			MgO					
			SiO_2					
	30	900	Mg_2SiO_4					
			MgSiO_3					
			MgO					
120	900	MgSiO_3	14	0.21	0.925	0.884	0.522	
		MgSiO_3	31	0.09	0.925	0.883	0.532	
$2\text{Mg}(\text{OH})_2 + \text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$	10	900	Mg_2SiO_4	25	0.17	1.020	0.598	0.476
			MgO	13	0.23	0.421		
			SiO_2					
	30	900	Mg_2SiO_4	29	0.14	1.020	0.598	0.475
			MgO	14	0.07	0.421		
			SiO_2					
120	900	Mg_2SiO_4	23	0.16	1.019	0.598	0.475	
		MgO	11	0.12	0.421			
		SiO_2						
	1200	Mg_2SiO_4	43	0.08	1.020	0.598	0.475	

during the solid-phase reaction dissolves in water and is easily removed. Thermograms of the washed samples (see Fig. 1) contain, in addition to the endothermic effect in the region of 130 °C, also an exothermal effect at 865 °C related to the crystallization of enstatite MgSiO_3 . Crystallite size and lattice parameters of this metasilicate at 900 °C are listed in Table 1. With further rise of the annealing temperature to 1200 °C, the transition into protoenstatite MgSiO_3 with an increase in crystallite size occurs.

The synthesis of magnesium metasilicate can be represented by the following scheme:



For the activation of a mixture of magnesium chloride and sodium metasilicate at a ratio of $\text{Mg}/\text{Si} = 2$, to implement the exchange reaction in full, it is necessary to involve additional sodium silicate, for example. Sodium chloride formed during the solid-phase reaction is recorded according to the X-ray data and thermographic ones (for example, see Fig. 1). On the basis of the composition of the mixture under activation, it may be assumed that two reactions occur in parallel: the first one is accompanied by the formation of NaCl and hydrated magnesium silicate of the type of $\text{MgO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$, while the second reaction results in the formation of NaCl and magne-

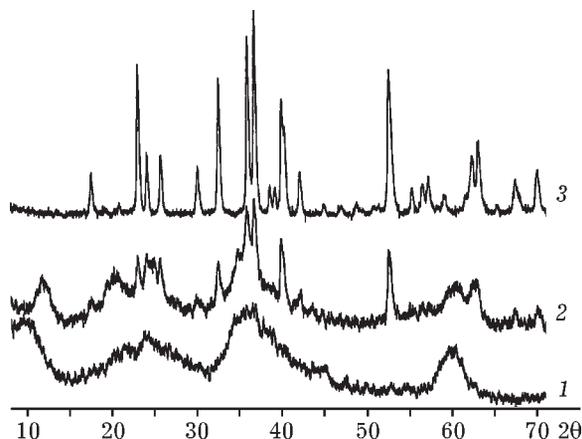
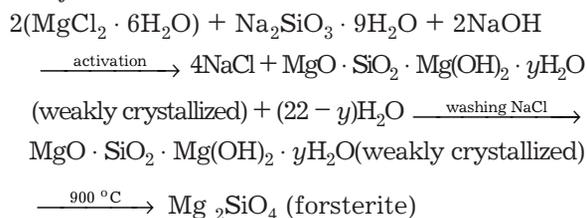


Fig. 3. X-ray diffraction patterns of the samples obtained by activation of the mixture $2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}) + \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} + 2\text{NaOH}$ and washed to remove NaCl (1), further annealed at 500 (2) and 900 °C (3).

sium hydroxide $\text{Mg}(\text{OH})_2$. However, the thermograms do not exhibit endothermic effect of dehydration at 410 °C, which is characteristic of magnesium hydroxide; the absorption band in the region of 3700 cm^{-1} related to the stretching vibrations of hydroxyl groups does not appear in the IR spectra. Therefore, magnesium is present in the formed silicate entirely in the bound state. In the diffraction patterns of the samples washed from sodium chloride (Fig. 3), one can observe a number of fuzzy reflections of low intensity in the region of $2\theta = 10\text{--}12, 20\text{--}22, 24, 36, 60^\circ$. In the thermograms of these samples, in addition to the endothermic effect related to the removal of weakly bound water at 130 °C, dehydration effect at 545 °C appears; it is accompanied by mass loss (see Fig. 1). The formed compound is likely magnesium hydrosilicate of the type $\text{MgO} \cdot \text{SiO}_2 \cdot \text{Mg}(\text{OH})_2 \cdot y\text{H}_2\text{O}$ or $\text{Mg}_2\text{SiO}_3(\text{OH})_2 \cdot y\text{H}_2\text{O}$. It follows from the data shown in Fig. 3 that magnesium orthosilicate Mg_2SiO_4 starts to be formed in the samples annealed at 500 °C. At 900 and 1200 °C only forsterite is observed. Its structural characteristics are listed in Table 1. The vibrational spectra of the samples with $\text{Mg}/\text{Si} = 2$ noticeably differ from those for the samples with $\text{Mg}/\text{Si} = 1$ (see Fig. 2). The washed samples exhibit an absorption band in the region of 900 cm^{-1} which can be assigned to the bending vibrations of Me-OH in the formed magnesium hydrosilicate $\text{MgO} \cdot \text{SiO}_2 \cdot \text{Mg}(\text{OH})_2 \cdot x\text{H}_2\text{O}$.

The observed transformations occurring during activation and thermal treatment of the indicated mixture can be represented schematically as follows:



The second series of samples was prepared through the activation of a mixture of magnesium hydroxide $\text{Mg}(\text{OH})_2$ and silica gel $\text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$. The degree of interaction between the components in this case is substantially dependent on the time of activation and the composition of samples. The data of thermal analysis of the samples with the ratio $\text{Mg}/\text{Si} = 1$ and 2 activated for 10 and 120 min are resented in Fig. 4. The endothermic effect in the region of 415 °C points to the presence of unreacted magnesium hydroxide. The content of free $\text{Mg}(\text{OH})_2$ decreases with an increase in activation time, so that it is almost absent from the sample with the initial composition $\text{Mg}/\text{Si} = 1$ after treatment for 120 min. To reveal the nature of the (X-ray amorphous) compound formed during the activation of the mixture of magnesium hydroxide and silica gel, we recorded the IR spectra for the maximal (120 min) activation time (Fig. 5). With an

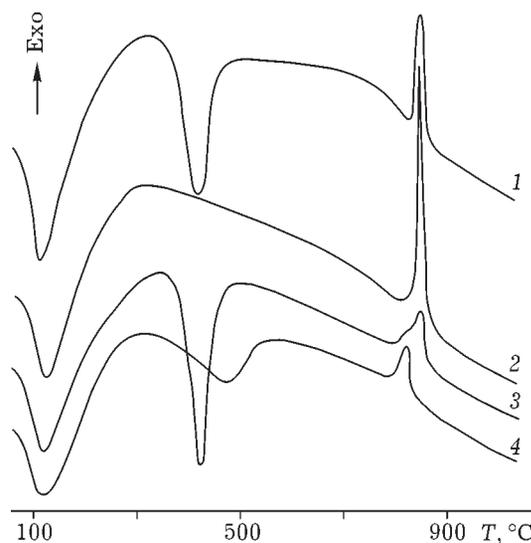


Fig. 4. DTA curves of the samples of mixture $\text{Mg}(\text{OH})_2 + \text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$ (1, 2) and $2\text{Mg}(\text{OH})_2 + \text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$ (3, 4) activated for 10 (1, 3) and 120 min (2, 4).

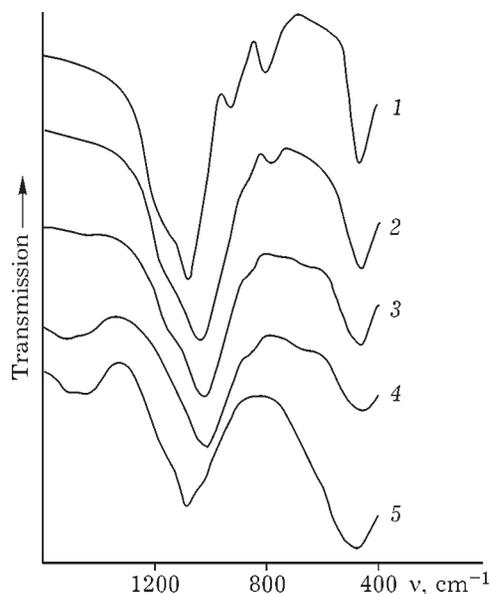
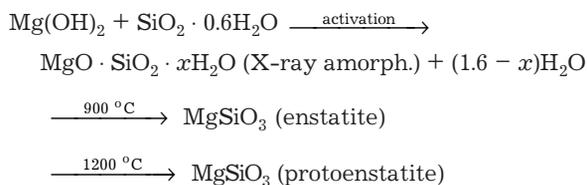


Fig. 5. IR spectra of the mixture $\text{Mg}(\text{OH})_2 + \text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$ with Mg/Si ratio equal to 0 (1), 0.3 (2), 0.6 (3), 1.0 (4), 2.0 (5) activated for 120 min.

increase in magnesium content in the samples having the composition $\text{Mg}/\text{Si} \leq 1$, we observe gradual decrease in the intensity of absorption bands at 800 and 830 cm^{-1} (characteristic of silica gel), an increase in the absorption in the region 600–700 cm^{-1} (stretching vibrations of $\text{Mg}-\text{O}$), while the band of stretching vibrations of $\text{Si}-\text{O}$ in the silicate framework undergoes monotonous shift to longer wavelengths. Insertion of magnesium into the silicate framework occurs, resulting in the formation of (X-ray amorphous) solid solution of the type $m\text{MgO} \cdot (1 - m)\text{SiO}_2 \cdot x\text{H}_2\text{O}$. This insertion is likely to have a limited character because even for the samples with the ratio $\text{Mg}/\text{Si} = 2$ the observed spectra differ substantially (see below). It should be noted that the IR spectra of the samples having the composition $\text{Mg}/\text{Si} = 1$ obtained in one and other series are identical (compare Fig. 2, curve 1 and Fig. 5, curve 4). On this basis, it may be assumed that the nature of the compounds formed both during the activation of the mixture of hydroxides and in the above-considered reactions is identical. X-ray amorphous compound $\text{MgO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$ gets transformed at 860 °C into enstatite, which is accompanied by the exothermal effect. The size of crystallites and the lattice parameters of MgSiO_3 are presented in Table 1. With further rise of annealing

temperature, the transition of enstatite into protoenstatite MgSiO_3 occurs (1200 °C). It should be noted that the initial (non-activated) mixture of magnesium hydroxide and silica gel ($\text{Mg}/\text{Si} = 1$) annealed at 1200 °C is only a mixture of crystal magnesium oxide and silicon dioxide (cristobalite).

The transformations observed during the activation for 120 min in the mixture of magnesium hydroxide and silica gel and subsequent thermal treatment can be represented in the following manner:

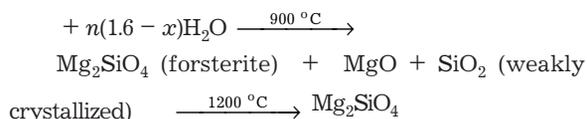
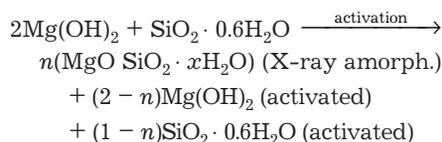


However, the situation becomes much more complicated in the presence of unreacted components in the system due to insufficient activation time. In the sample activated for 10 min, after thermal treatment at 900 °C we observe the formation of forsterite Mg_2SiO_4 , magnesium oxide MgO and silicon dioxide SiO_2 . The latter is present in the ultrafine state and manifests itself in the X-ray diffraction patterns as a sole but very broad reflection with the maximum $2\theta = 21\text{--}23^\circ$. The sample activated for 30 min and thermally treated under the same conditions contains, in addition to the above-indicated compounds, also enstatite phase (see Table 1). Only activation for 120 min leads under these conditions to the formation of the sole compound, which is magnesium metasilicate MgSiO_3 .

For samples with relatively high magnesium content ($\text{Mg}/\text{Si} > 1$), the transformations generally are noticeably different. Two bands related to the stretching vibrations of the silicate framework are observed in the IR spectra of the sample with the ratio $\text{Mg}/\text{Si} = 2$ activated for 120 min: 1020 and 1090 cm^{-1} . The former band is due to the formation of the solid solution ($\text{MgO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$), while the latter one appears due to the unreacted hydrated silicon dioxide (see Fig. 5). The band at 3690 cm^{-1} in these spectra provides the evidence of the presence of unreacted magnesium hydroxide in the sample under investigation. This may be connected with partial limited insertion of magnesium into the spatial framework of silica gel. The diffraction patterns of all the samples of

activated mixture $2\text{Mg}(\text{OH})_2 + \text{SiO}_2 \cdot 0.6\text{H}_2\text{O}$ contain the reflections of unreacted magnesium hydroxide. In the sample activated for 120 min, this hydroxide ($a = 0.313 \text{ nm}$, $c = 79 \text{ nm}$) is present in the ultrafine state with the average crystallite size $d = 11 \text{ nm}$. The endothermic effect of its dehydration shifts from $410 \text{ }^\circ\text{C}$ for the samples activated for 10–30 min to $455 \text{ }^\circ\text{C}$ (see Fig. 4). Exothermal effects in the region $825\text{--}860 \text{ }^\circ\text{C}$ are due to the crystallization of the formed compounds and depend on the time of mixture activation. After thermal treatment at $900 \text{ }^\circ\text{C}$ the reflections of forsterite Mg_2SiO_4 , magnesium oxide MgO and silicon dioxide SiO_2 appear in the diffraction patterns of all the samples. The latter component is present even in the ultrafine state and manifests itself as a broad reflection with the maximum at $2\theta = 21\text{--}23^\circ$. One can clearly see an increase in the amount of formed forsterite and a decrease in the amount of unreacted oxides with an increase in activation time. After thermal treatment at $1200 \text{ }^\circ\text{C}$, only in the sample activated for 120 min we observe complete interaction between the components resulting in the formation of the sole product – magnesium orthosilicate (see Table 1). It should be stressed that only crystal magnesium oxide and silicon dioxide (cristobalite) are formed in the non-activated mixture ($\text{Mg}/\text{Si} = 2$) subjected to thermal treatment under the same conditions at $1200 \text{ }^\circ\text{C}$.

The scheme of the transformations observed in the sample activated for 120 min can be represented in the following manner:



CONCLUSION

Investigations show that for the same method of mechanical activation of solid mixtures the exchange reactions between salt reagents proceed much more efficiently than the interaction between magnesium hydroxide and silica gel. Independently of the initial components, the first stages lead to the formation of (X-ray amorphous) solid solutions having the composition $\text{MgO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$ ($\text{Mg}/\text{Si} \leq 1$). The formation of these solid solutions in aluminosilicate mixtures was demonstrated by us previously for the synthesis of mullite using the mechanochemical method [5]. For the components ratio in the mixture $\text{Mg}/\text{Si} = 2$, as a consequence of different degree and form of magnesium binding, non-identical routes of the formation of the same final crystal product are realized. Magnesium metasilicate (enstatite) and magnesium orthosilicate (forsterite) formed as a result of mechanical activation followed by thermal treatment are composed of nanometer-sized crystallites.

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