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СИНТЕЗ МАГНЕЗИОХРОМИТА ($MgCr_2O_4$): ВЛИЯНИЕ ПРЕДВАРИТЕЛЬНОЙ МЕХАНИЧЕСКОЙ И МИКРОВОЛНОВОЙ ОБРАБОТКИ ПРЕКУРСОРОВ

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Исследован процесс синтеза магнезиально-хромитовой шпинели, исходя из оксидов, гидроксидов и нитратов магния и хрома. Сопоставлена реакционная способность прекурсоров с помощью эффективных констант скорости, рассчитанных по уравнению Гинстлинга-Броунштейна. Возможность использования данного уравнения подтверждена прямолинейностью зависимостей в его координатах с высоким коэффициентом линейной аппроксимации. Сопоставлена активность различных форм оксида магния (мягко обожженного, или каустического магнезита, и намертво обожженного, или периклаза) в реакции шпинелеобразования. Оксидные прекурсоры, особенно с участием периклаза, взаимодействовали между собой с существенно меньшей скоростью по сравнению с гидроксидами и солями. Проанализировано влияние предварительной механоактивации ударно-истирающим и истирающим способом в планетарной и шаро-кольцевой мельнице соответственно, а также микроволновой обработки (2,45 ГГц). Наибольшее положительное влияние обработки в планетарной мельнице, связанное с активизацией соединений Mg и Cr, проявлялось в области относительно низких температур (700-1100 °С). Например, при температуре 1000 °С выход магнезиохромита при совместной ударной обработке оксидов был в ~ 2 раза выше, чем при простом смешении. При дальнейшем повышении температуры влияние предварительной обработки уменьшалось, поскольку в этих условиях возрастали коэффициенты диффузии, обеспечивающие сравнительно быстрое протекание реакции и без МО. Отмечено заметное снижение активности оксида магния в реакции шпинелеобразования после истирающей обработки в шаро-кольцевой мельнице, связанное со скольжением плоскостей в кристаллах кубической сингонии и приводящее к обнажению плоских поверхностей. В результате этого в наибольшей степени нарушенный дефектный слой удалялся с зерен. Установлено, что наиболее эффективен комбинированный способ, состоящий из механической обработки (МО) смеси нитратов магния и хрома в планетарной мельнице и последующего обжига в термической печи (1000 °С), который приводил к образованию практически монофазного продукта. Микроволновая обработка занимала по результативности промежуточное положение.

Ключевые слова: шпинель, магнезиохромит, $MgCr_2O_4$, твердофазный синтез, кинетика шпинелеобразования, механоактивация, микроволновая обработка, каустический магнезит, периклаз

MAGNESIOCHROMITE ($MgCr_2O_4$) SYNTHESIS: EFFECT OF MECHANICAL AND MICROWAVE PRETREATMENT

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Magnesiochromite spinel synthesis based on oxides, hydroxides and nitrates of magnesium and chromium was investigated. The precursors reactivity was compared by means of effective rate constants calculated by Ginstling-Brounshtein equation. The possibility of use of this

equation was confirmed by the dependences linearity with high linear approximation coefficients. The reactivity of MgO various forms (soft-burned, or caustic magnesite, and dead-burned, or periclase) in the spinel formation was compared. Oxide precursors (especially with the periclase participation) reacted with the substantially less rate in comparison with hydroxides and salts. The influence of a preliminary mechanical activation by impact-and-attrition (planetary mill) and attrition (ball-ring mill) action as well as a microwave treatment (2.45 GHz) was analyzed. The most positive effect of a mechanical treatment in a planetary mill that was associated with an activation of Mg and Cr compounds became apparent in the field of relatively low temperatures (700-1100 °C). For example, $MgCr_2O_4$ yield at 1000 °C and the joint impact treatment of oxides was twice as much than under the simple mixing. The subsequent temperature rising lead to some decrease of a pretreatment effect so long as diffusion coefficients in these conditions grew, so the reaction run rapidly even without a preliminary mechanical treatment. It was noticed that an appreciable reduction of MgO reactivity in the spinel formation after a certain attrition in a ball-ring mill linked to the plane sliding in cubic crystals and resulted in the removing of the most disordered and defective layer from grains and the plane surface uncovering. The combined method consisting of a mechanical treatment of magnesium and chromium nitrates mixture in a planetary mill and the subsequent burning in a thermal kiln (1000 °C) was considered as the most effective as it resulted in practically single product. The microwave treatment took up an intermediate position by the effectiveness.

Key words: spinel, magnesiochromite, $MgCr_2O_4$, solid-phase synthesis, spinel formation kinetics, mechanical activation, microwave treatment, caustic magnesite, periclase

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INTRODUCTION

Magnesiochromite $MgCr_2O_4$ is the only compound in the system MgO – Cr_2O_3. It attracts the attention because of its unique physical and chemical properties and technological possibilities. This spinel is used in some refractories' composition [1, 2], semiconductors [3], magnetic and electrical materials [4], sensors [5], catalysts [6-8], photocatalysts [9], pigments [10], etc. Active work on nanoceramics and nanocomposites with $MgCr_2O_4$ participation [8, 9, 11-14].

Magnesium chromite is synthesized by means of different ways, namely: ceramic synthesis [15, 16], co-precipitation [7], sol-gel method [3, 6], combustion [11], hydrothermal method [12], zone melting [4], co-crystallization [17], etc. At the same time, solid-phase synthesis remains as the main industrial mode. It provides the interaction of magnesium and chromium oxides. The necessary temperature for reaction realization is between 1100 and 1600 °C. This process is long and power-intensive, so it sometimes accompanied by a mechanical (MT) or microwave treatment (MWT).

The mechanical activation is a well-known method of the reactivity increase for many different substances and materials including those for obtaining of magnesia spinel [18], chromites [19, 20]. Mechanochemical reactions are mostly realized in high-energy planetary mills with impact-attrition action. The microwave synthesis of compound oxides is studied to a lesser extent [21, 22].

The present study mainly concerns the effects of a microwave and different mechanical pretreatments on $MgCr_2O_4$ ceramic synthesis. There were chosen magnesium and chromium oxides, hydroxides and salts (nitrates) as precursors. Despite many executed works the juxtaposition of different oxides sources behavior in equivalent conditions are practically absent. There were chosen a ball-ring mill with attrition action and a planetary mill in which an impact and attrition actions of grinding bodies are combined.

MATERIALS AND EXPERIMENTS

The reagents Cr_2O_3, $Cr(OH)_3$, $Cr(NO_3)_3\cdot 9H_2O$, $Mg(OH)_2$, $Mg(NO_3)_2\cdot 6H_2O$ employed in this study were analytical grade with the averaged particle size no more than 10 μm. The reactive magnesium oxide (caustic magnesite, 99.7 wt % MgO) and sintered periclase (China, 96.8 wt % MgO) were also used as sources of magnesium oxide. The relative amounts of MgO and Cr_2O_3 were chosen to be equal to the composition of $MgCr_2O_4$.

A mechanical treatment of mixtures for 20 min was carried out in a ball-ring mill (BRM) with steel balls 25.4 mm in diameter and in AGO-2 planetary mill (PM) with corundum grinding bodies. A microwave treatment for 15 min was done in a magnetron oven BOSCH HMT72M420 (2,45 GHz, 6 kW).

XRD-patterns were obtained using a diffractometer DRON-6 with a copper target ($\lambda = 1.54$ Å), a graphite diffracted beam monochromator, and a working voltage and current of 40 kV and 100 mA, respectively.

XRD peaks for 2θ 18.1, 36.1, 57.5 and 63.3 correspond to cubic lattice planes of magnesiochromite (110), (311), (511) и (440), respectively (JCPDS, 10-0351). The quantitative XRD analysis was made analyzing magnesiochromite reflexes, which are pretty much isolated from lines of accompanying compounds (chromium and magnesium oxides).

MgO atomic-force microscopy (AFM) images were taken using an atomic-force microscope Solver P47-PRO (NT-MDT, Russia) at room temperature in air. Semicontact method of the surface scanning with a standard silicon pyramidal cantilever was used; scanning area was 50×50 μm.

Specific surface area (SSA) measurements were run on Autosorb-1 Quantachrome. Powder samples (0.4 g) were degassed under vacuum for 8 h and a 10-point analysis was conducted at 77 K in liquid N_2 over a relative pressure range of 0.05-0.33 p/p_o. SSAs were determined using Brunauer-Emmett-Teller (BET) method.

Reactive mixtures for spinel formation kinetics studying were prepared by components mixing and subsequent cold pressing under 200 MPa in the presence of a lignosulfonate technical as a temporary binder. Tablets were burned in a resistance-heating furnace MP 2UM and MF-1700M (800-1500 °C).

RESULTS AND DISCUSSION

Oxides, hydroxides and salts (nitrates) were chosen to compare the precursors reactivity. Fractional conversion values ($MgCr_2O_4$ spinel content) α under various synthesis duration τ were treated according to Ginstling-Brounshtein equation:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=k_{GB}\tau,$$

where k_{GB} – effective rate constant, s^{-1}.

The possibility of its use was confirmed by the dependence's linearity with high linear approximation coefficients (0,96-0,99).

The reactivity of MgO various forms in the spinel formation was compared. Soft-burned, or caustic magnesite is obtained by the burning at 600-1000 °C whereas periclase (dead-burned magnesite) is produced above 1450 °C.

The first MgO is a friable powder which has the density about 2.3 g/sm^3, rather big specific surface and reactivity from high to medium. MgO produced under a hard burning has medium crystallites dimensions and the lower activity because of lower specific surface.

Dimensions of caustic magnesite and periclase crystallites calculated by Debay-Sherrer equation were 28 ± 5 и 116 ± 8 nm, respectively. As a result, the activity of the second compound was considerably lower (Table 1).

Table 1

Effective rate constants of $MgCr_2O_4$ formation from different precursors (1000 °C)

***Таблица 1.* Эффективные константы скорости реакции образования $MgCr_2O_4$ из различных прекурсоров (1000 °C)**

Precursors	Effective rate constant $k_{GB}\cdot10^5$, s^{-1}
MgO (caustic magnesite) + Cr_2O_3	0.81 ± 0.04
MgO (periclase) + Cr_2O_3	0.25 ± 0.04
$Mg(OH)_2$ + Cr_2O_3	3.8 ± 0.4
$Mg(OH)_2$ + $Cr(OH)_3$	15 ± 1
$Mg(OH)_2$ + $Cr(NO_3)_3$	18 ± 1
$Mg(NO_3)_2$ + $Cr(NO_3)_3$	29 ± 2

Oxides precursors react more slowly as compared with hydroxides and salts. During hydroxides and nitrates pyrolysis every substance is in an active state because of incipient strains and following lattice trnsformation (Hedwall effect). The lattice becomes temporarily unstable that raises the reaction rate. Thus, from now on, we used magnesium and chromium hydroxides and nitrates for spinel synthesis.

XRD-patterns of burned product (800 °C) from mixtures $Mg(OH)_2$ and $Cr(OH)_3$ obtained by a simple mixing and after mechanical treatment in a ball-ring mill and in a planetary mill are presented in Fig. 1.

In all cases there was formed the desired product (magnesiochromite $MgCr_2O_4$) in every studied system but the content of initial oxide phases (MgO, Cr_2O_3) was large especially under a simple mixing: 100% peak corrisponded to Cr_2O_3 (Fig. 1, *а*). After a mechanical pretreatment, maximum peak belonged to the spinel (Fig 1, *б*-*в*). The more intensive influence in PM allowed the obtaining of the greater product quantity. During a mechanical treatment layer structures of hydrixides began to destroy and form reactive oxides. Dependences (Fig 2) define the spinel accumulation in reaction mixtures under various temperatures and treatment modes.

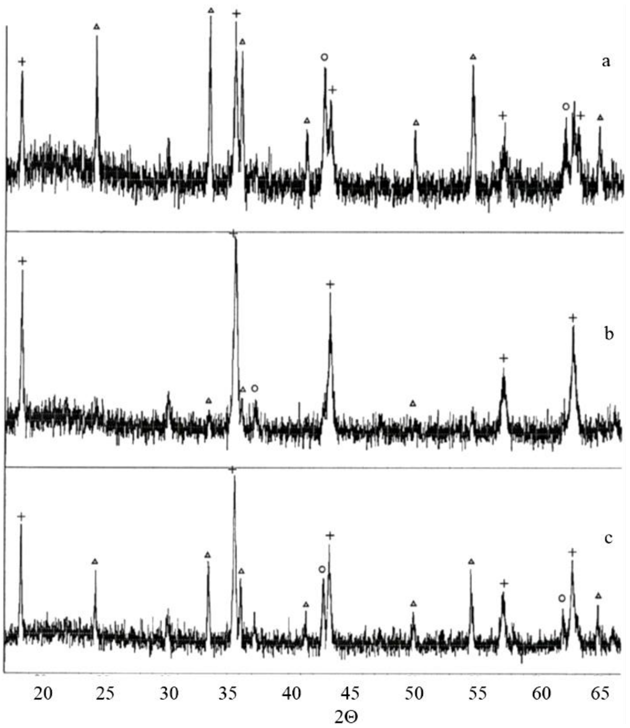
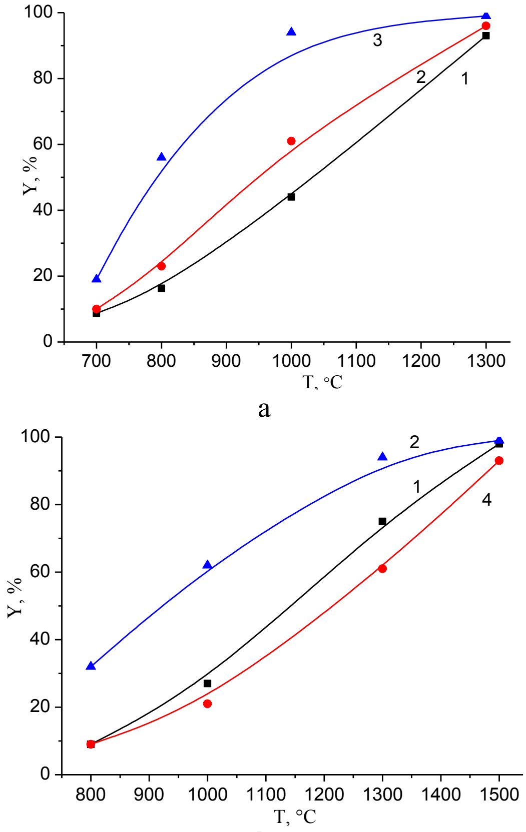


Fig. 1. XRD-patterns of burned product (800 °C, 1 h) from $Mg(OH)_2$ and $Cr(OH)_3$ mixtures, obtained with no mechanical treatment (a), after treatment in BRM (b) and PM (c) + $MgCr_2O_4$; Δ Cr_2O_3; ○ MgO

Рис. 1. Дифрактограммы продукта обжига (800 °C, 1 ч) смесей $Mg(OH)_2$ и $Cr(OH)_3$, полученных без МО (a), обработкой в ШКМ (b) и ПМ (c) + $MgCr_2O_4$; Δ Cr_2O_3; ○ MgO

The most positive MT influence in a planetary mill (Fig. 2, curves 2) connected with Mg and Cr compounds activation became apparent at rather low temperatures (700-1100 °C). For example, at 1000 °C magnesiochromite yield after the joint impact component treatment was twice as much than under the simple mixing (Fig. 2, b). At the further temperature rising curves 1 and 2 (Fig. 2) approached each other, so the influence of a pretreatment diminished, as the diffusion coefficients which supported the rather fast reaction also with no MT raised in these conditions. The similar dependences character was received under $MgAl_2O_4$ synthesis investigation [18].

The joint mechanical treatment always accelerates the spinel formation. An appreciable reduction of MgO reactivity in this reaction after a certain attrition in a ball-ring mill that was described earlier [23, 24] was linked to the plane sliding in cubic crystals and resulted in the removing of the most disordered and defective layer from grains and the plane surface uncovering. AFM-images confirmed this character of surface topography changes and its roughness after various treatments. To estimate the roughness, we eliminated the general background irregularity by means of the subtraction of the plane/surface (in this case, a cubic surface). Such corrected images (Fig. 3) showed that polycrystals after an attrition in ball-ring mill had the minimal roughness (Fig. 3, b). After an impact treatment (Fig. 3, c) the surface was obvious irregular. Calculated summary roughness of MgO particles diminished after an attrition: ~1 nm at the distance 1.5 μm instead of 15 nm at the distance 8 μm.



a

b

Fig. 2. Influence of temperature and treatment mode of reaction mixtures $Mg(OH)_2 + Cr(OH)_3$ (a), $MgO + Cr_2O_3$ (b) upon the spinel yield: 1 – simple component mixing; 2 – joint component pretreatment in PM; 3 – joint component attrition in BRM; 4 – MgO attrition in BRM before components mixing

Рис. 2. Влияние температуры и способа подготовки реакционных смесей $Mg(OH)_2 + Cr(OH)_3$ (a), $MgO + Cr_2O_3$ (b) на выход шпинели: 1 – простое смешение компонентов; 2 – предварительная совместная обработка компонентов в ПМ; 3 – совместное истирание компонентов в ШКМ; 4 – истирание MgO в ШКМ перед смешением компонентов

$Mg(OH)_2 + Cr(OH)_3$, $Mg(NO_3)_2 + Cr(OH)_3$, $Mg(OH)_2 + Cr(NO_3)_3$ and $Mg(NO_3)_2 + Cr(NO_3)_3$ mixtures with stoichiometric relationships of components were exposed to a microwave treatment (MWT). XRD-patterns of products testified an amorphous character of all treated mixtures. So, there were happened essential changes in compounds lattices during

MWO which were accompanied with defect accumulation. Indicated above precursor mixtures after MWT were subjected to the traditional burning in a thermal oven at 1000 °C. Fig. 4 shows XRD-patterns for products.

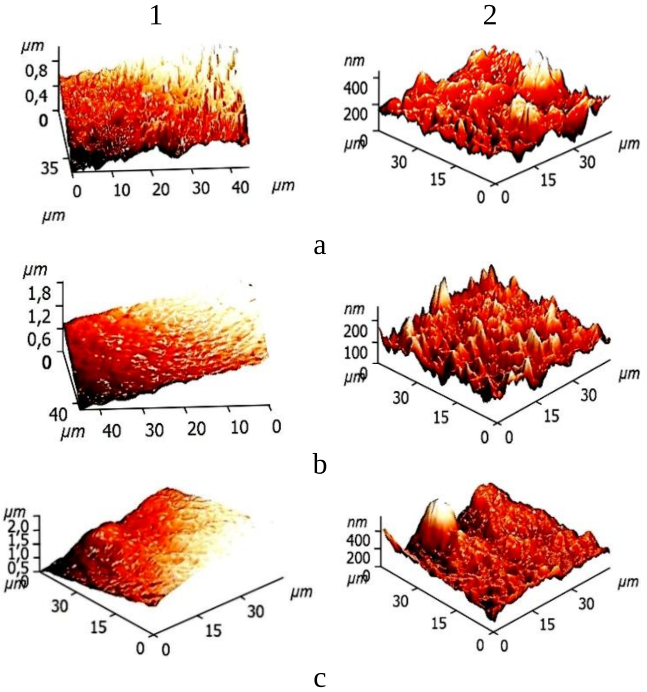


Fig. 3. AFM-images of MgO polycrystals (within one grain) with no mechanical treatment (a), after treatment in BRM (b) and PM (c); 1 – initial image, 2 – 3-order surface substracted

Рис. 3. АСМ-изображения поликристаллов MgO (в пределах одного зерна): a – без обработки; b – после обработки в ШКМ; c – после обработки в ПМ; 1 – исходное изображение, 2 – после вычитания поверхности 3-го порядка

Flat areas kept this state also under high temperatures. By this reason, $MgCr_2O_4$ formation intensity after such treatment decreased in all temperature range (Fig. 2, b, curve 4).

Findings testified $MgCr_2O_4$ formation when reaction mixtures were composed from all precursor pairs. In all cases100% peaks corresponded to the spinel. The burned product from $Mg(OH)_2$ + $Cr(OH)_3$ mixture was the least crystallized (Fig. 4, a). Besides, it contained a considerable amount of Cr_2O_3. It is difficult to isolate MgO peaks because of their close arrangement to spinel reflexes: interplanar spacings are equal to 0.211 and 0.149 nm for MgO (100%); 0.209 and 0.147 nm (54 and 47% respectively) for $MgCr_2O_4$. The maximum peak (100%) for spinel revealed independently (d = 0.251 nm). The burned products from other mixtures were rather well crystallized (Fig. 4, c-d). However, magnesiochromite was practically single product only under the choice of Mg and Cr nitrates as precursors. The last fact was also confirmed by element analysis data.

The $MgCr_2O_4$ yield values for various pretreatment modes of reaction mixtures before the burning are compared in Table 2. The maximum yield was observed when Mg and Cr nitrates were used. Every kind of their activation raised the spinel yield up to 92-100%. Evidently, it related to a high hydration degree of initial nitrates, so MT and MWT lead to considerable changes in compound structures during the water elimination. The intensive mechanical treatment in a planetary mill was the most effective one for all mixtures. During an impact action, reagent crystallites accumulated a big quantity of vacancies including as the dehydration result. An attrition treatment in a ball-ring mill was accompanied by substantially smaller power inputs; it was too little efficacious.

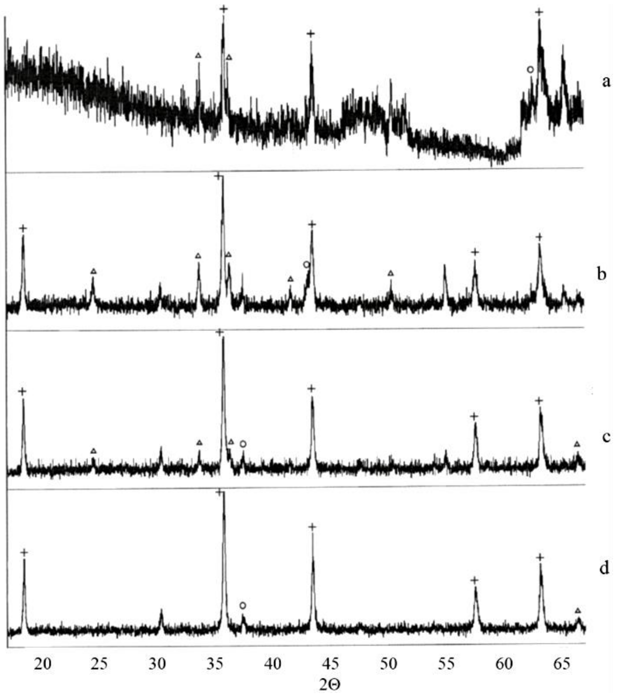


Fig. 4. XRD-patterns of mixtures subjected to the microwave treatment and the burning in a thermal oven (1000 °C, 1 h): a - $Mg(OH)_2$ and $Cr(OH)_3$; b - $Mg(NO_3)_2$ and $Cr(OH)_3$; c - $Mg(OH)_2$ and $Cr(NO_3)_3$; d - $Mg(NO_3)_2$ and $Cr(NO_3)_3$

Рис. 4. Дифрактограммы смесей, подвергнутых микроволновой обработке и обжигу в термической печи (1000 °C, 1 ч): a - $Mg(OH)_2$ и $Cr(OH)_3$; b - $Mg(NO_3)_2$ и $Cr(OH)_3$; c - $Mg(OH)_2$ и $Cr(NO_3)_3$; d - $Mg(NO_3)_2$ и $Cr(NO_3)_3$

The combined method consisting of a mechanical treatment of magnesium and chromium nitrates mixture in a planetary mill and the subsequent burning in a thermal kiln (1000 °C) was considered as the most effective as it resulted in practically single product. The microwave treatment took up an intermediate position by the effectiveness.

Table 2

$MgCr_2O_4$ yield from mixtures pretreated by microwave and mechanical methods after the burning (1000 ^oC, 1 h)

***Таблица 2.* Выход $MgCr_2O_4$ из смесей, подвергнутых предварительной микроволновой и механической обработке, после обжига (1000 °С, 1 ч)**

Precursors	Spinel yield, %, with no treatment	Spinel yield, %, after treatment		
		in microwave oven	in BRM	in PM
$Mg(OH)_2$+$Cr(OH)_3$	44 ± 3	58 ± 3	61 ± 2	94 ± 5
$Mg(OH)_2$+$Cr(NO_3)_3$	53 ± 4	79 ± 5	58 ± 3	97 ± 6
$Mg(NO_3)_2$+$Cr(OH)_3$	56 ± 2	72 ± 8	61 ± 4	98 ± 5
$Mg(NO_3)_2$+$Cr(NO_3)_3$	61 ± 5	100 ± 3	92 ± 3	100 ± 4

The burning temperature rising lead to some healing of defects; crystallites sizes became bigger (Table 3).

Table 3

Structural characteristics of magnesiochromite from burned mixtures of Mg and Cr nitrates after treatment in planetary mill

***Таблица 3.* Структурные характеристики магнезиохромита из обожженной смеси нитратов Mg и Cr после обработки в планетарной мельнице**

Burning temperature, °C	Size of crystallites, nm	Cell parameter a, nm	Specific surface, m^2/g
800	17.7	0.8519 ± 0.0003	63.3 ± 0.4
1000	23.9	0.8496 ± 0.0004	51.6 ± 0.3
1200	35.5	0.8484 ± 0.0004	21.2 ± 0.3
1400	51.0	0.8461 ± 0.0005	17.1 ± 0.1

Some structural ordering brought to the cell parameter diminution approaching to the theoretical value (0.8329 nm). It was naturally followed by the reduction of the product specific surface.

CONCLUSION

Reactive mixtures were activated by means of a mechanical and microwave treatment to intensify the magnesiochromite ceramic synthesis. The spinel yield after burning under relatively low temperature (1000 °C) increased up to 92-100%. The single-phase $MgCr_2O_4$ was synthesized from the mixture of Mg and Cr nitrates. An attrition of the single MgO before the spinel formation made the oxides interaction slower that was confirmed with a lesser quantity of the formed product. The reactivity of different precursors (oxides, hydroxides, salts of Mg and Cr) during the spinel formation was juxtaposed by means of effective rate constants.

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