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## ТЕХНОЛОГІЯ ОСОБЛИВОСТІ СИНТЕЗУ ПОРОШКІВ ФОРСТЕРИТОВОГО СКЛАДУ

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Розроблено технологічні основи синтезу форстеритового порошку золь-гель методом. Показано доцільність використання як магнійвмісного компонента кристалогідрату  $Mg(CH_3COO)_2 \cdot 4H_2O$  через найменшу тривалість гелеутворення розчину. Методами ДТА і РФА встановлено температуру початку форстеритоутворення гель-порошків (700 °C). Показана можливість її зниження на 100 °C введенням флюорвмісних мінералізаторів. Найефективнішим є використання водорозчинного мінералізатора  $H_2SiF_6$ , що підтверджується наявністю екзо ефектів за нижчих температур. Встановлено технологічні параметри отримання монофазних порошків форстериту. Методом РФА встановлено фазовий склад порошку. Наведено технологічну схему отримання форстериту.

Ключові слова: форстерит, керамічні нанодисперсні порошки, мінералізатори, модифікування, золь-гель метод, форстеритоутворення.

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## TECHNOLOGICAL FEATURES OF FORSTERITE CONTAINING POWDERS SYNTHESIS

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Technological basics of forsterite powder synthesis by sol-gel method was developed. The expedience of use as a magnesium containing component of crystalline  $Mg(CH_3COO)_2 \cdot 4H_2O$  due to the least duration of gel formation was shown. The temperature of the beginning of forsterite formation gel powder was determined by DTA and XRD methods (700 °C). The possibility of its reduction to 100 °C by introducing fluoride containing mineralizators was shown. The most effective is the use of a water-soluble mineralizator  $H_2SiF_6$ , it is confirmed by the presence of ekzo effects at lower temperatures. Technological parameters of monophasic forsterite powders obtention was established. The phase composition of the powder was done by the XRD method. The technological scheme of the forsterite obtention was shown.

Key words: forsterite, ceramic nanoparticle powders, mineralizators, modification, sol-gel method, forsterite formation.

Formulation of the problem and its connection with important scientific goals. Modern development of many industries, including vacuum, optical, laser, electronic, sensory requires the development of new high-performance materials. Among them special attention is focused on ceramics

from powders of refractory compounds, which differ due to the high reactive activity towards sintering. Ceramic materials obtained from such powders are characterized by high mechanical, thermal, electro, magnetic and other unique properties. For the production of high quality ceramics should be used non- aggregated ultrafine powders with spherical particles, whose size ranges from 10 to 100 nm. This ensures their mobility, lack of agglomeration, manufacturability etc [1, 2].

The synthesis of ceramic ultra powders is done by various methods, which often are complex, labor-intensive and energy-consuming. Today ones of the most promising chemical synthesis methods that allow to receive non-aggregated powders of given chemical composition, grain size of specific morphology [2]. It should be noted that this applies inexpensive raw materials and chemical materials. The main methods of obtention chemical powders are the deposition from solutions, hydrothermal and sol-gel methods.

Sol-gel method allows to obtain powders of different metal alkoxides mixtures at relatively low temperatures. These powders are chemically pure, characterized by uniform particle size and uniform distribution of several phases in the matrix [3]. The initial materials for the sol-gel process are soluble salts oxysalts and metal alkoxides.

Forsterite ceramics is one of the representatives of oxide ceramic materials that has broad application prospects, particularly for electro and radio ceramics, for the production of phosphors, high quality insulators, frames and covers of electron beam tubes, in medicine for the manufacture of ceramic implants [4]. Forsterite materials are characterized by the stability of the structure during the thermal treatment, great radiation resistance, high temperature coefficient of linear expansion etc. [5].

**Analysis of recent research and publications.** The obtention of dense crystalline ceramics based on forsterite is rather a difficult task. The production of such ceramics by the usual traditional technology, which includes a preliminary synthesis of forsterite from natural raw materials or high-pure silicon and magnesium oxides is a difficult way. In addition, the sintering temperature of such materials is high (about 1800 °C).

Today for the obtention of forsterite ceramics the high quality powders are used prepared by sol-gel method [6]. It should be noted that in this way there are different: initial materials (metal salt solutions, soluble hydroxides, alkoxides, salt solutions in combination with organic polymers etc.), environment (water, ammonia solution), gelation mechanism etc [7–11]. The temperature of forsterite powders synthesis by sol-gel method is below 1000 °C [8, 9].

It is known that one of the most promising way to reduce the burning temperature is input in a small amount of additives-mineralizers. According to [12] mineralizers not only accelerate the process of the mineralization, but also partly included in the composition of the formed minerals. The most effective additives are fluoride containing ones, including NaF, CaF<sub>2</sub>, MgF<sub>2</sub>, H<sub>2</sub>SiF<sub>6</sub> and others. Fluoride ions reduce the melt viscosity, facilitating the rapid crystal growth [13].

**The aim of work** – development of optimal technological conditions of sol-gel synthesis of forsterite powders modified by F<sup>-</sup>.

**Results and discussions.** For the synthesis of forsterite powder of composition 2MgO·SiO<sub>2</sub> ethyl silicate ETS-40 and hydrated magnesium acetate Mg (CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O were used as initial materials.

For obtention of pure oxygen containing powders previously ETS-40 was slowly hydrolyzed in the presence of hydrochloric acid at the ratio of components  $n\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{O} \geq 3$ . It should be noted that the temperature of initial components greatly influences on the exothermic process of ethyl silicate hydrolysis and can initiate the condensation at the beginning of hydrolysis that leads to the rapid coagulation and separation of the hydrolyzate [14]. Therefore, according to data [15] initial components were cooled to the temperature of 5–10 °C. Due to this the exothermic effect of hydrolysis decreases, allowing to carry out the whole stage of the reaction.

For gels obtention initial materials were mixed in the desired ratio according to the scheme shown in Fig. 1.

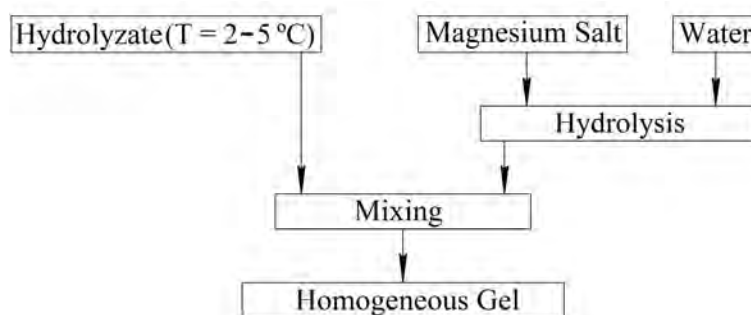


Fig. 1. The scheme of the homogeneous gel system  $MgO-SiO_2$

According to the results of previous studies [16] it was found that the pH and concentration of the initial solution significantly affect on the duration of gelation. In particular, changes in the concentration of the initial solution from 1 to 0.5 mol/l leads to an increase of the duration of gelation about 2.5 times and is 65 minutes at the maximum pH 6.78. Therefore, further studies were conducted based on solutions with concentration of 0.7 mol/l.

The obtained gels were kept at the room temperature for 2–3 days and dried at  $115 \pm 1$  °C within 35–40 hours. Phase composition of dried gels was investigated by X-ray diffraction analysis. As a result of studies it was found that the powder is X-ray amorphous, because there are no clear maxima on the diffractogram except the two “Halo” in  $2\theta = 10$  and  $24^\circ$  (Fig. 2).

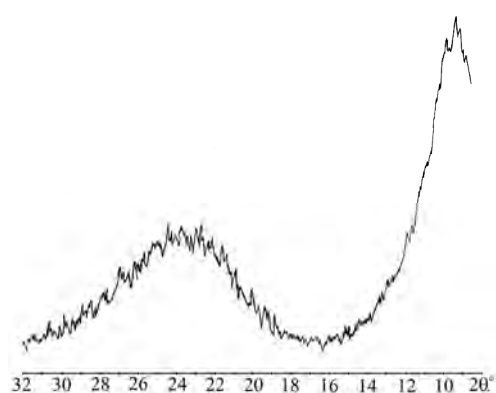


Fig. 2. The diffractogram of xerogel

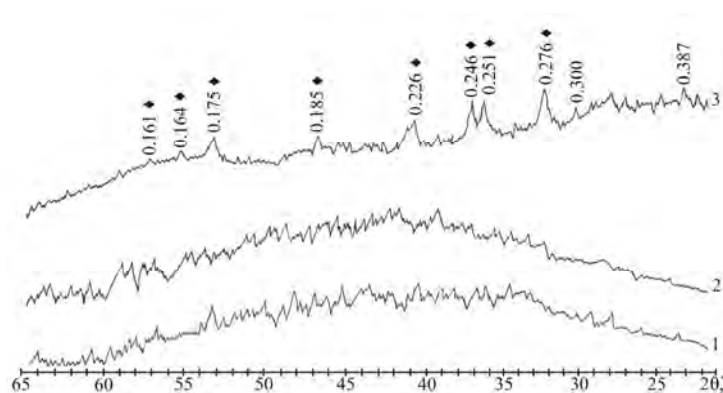


Fig. 3. Powder diffractograms, burned at the temperatures ( °C):  
1 – 500; 2 – 600; 3 – 700;  
♦ – enstatite ( $MgSiO_3$ ); without marking – forsterite

The obtained xerogels were burned at temperatures of 500–900 °C with steps of 100 °C with the 2 hours holding at the maximum temperature.

The X-ray analysis of powders (Fig. 3, curves 1 and 2) burned at temperatures of 500 and 600 °C, shows their amorphous structure. Powders synthesized at 700 °C (Fig. 3, curve 3) contain a small amount of forsterite ( $d/n$  0,387; 0,300). The increase of burning temperature to 800 and 900 °C leads to significant phase changes in powders (Fig. 4, curves 1 and 2). In particular, in the powder obtained at 900 °C, the amount of periklaz decreases approximately 75 %.

One of the ways of reduction of the minerals formation temperature is the activation of the powder mix by adding mineralizers. Thus the effectiveness of the additives is determined by their nature,

concentration and the distribution in the matrix [12]. In this work fluoride containing additives different by their nature in the form of magnesium fluoride  $MgF_2$  and hexafluorosilic acid  $H_2SiF_6$  were used as mineralizers in the amount of 4 wt. % and 4 vol. % respectively.

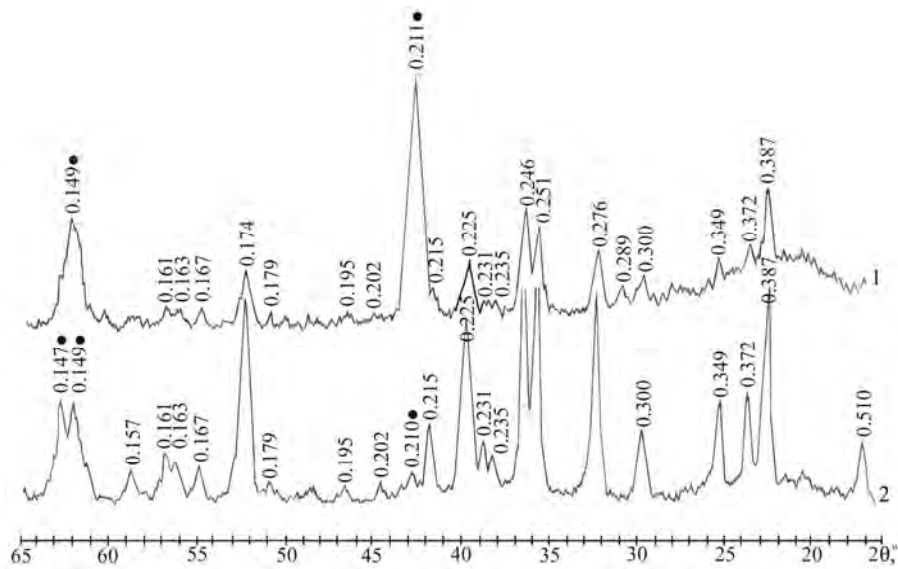


Fig. 4. Powder diffractograms, burned at the temperatures ( °C): 1 – 800; 2 – 900  
 ◆ – enstatite ( $MgSiO_3$ ); without marking – forsterite

The results of the studies show that the introduction of the mineralizator containing  $F^-$  ion, forsterite formation is observed at the temperature of 600 °C. The amount of formed forsterite is much greater compared to the powder obtained without the mineralizator. According to the differential thermal analysis (Fig. 5) the crystallization of forsterite finishes at the temperature of 900 °C, and the use of  $H_2SiF_6$  as a mineralizator causes the increase of exo effect and its displacement to lower temperatures. This is confirmed by the X-ray diffraction analysis that indicates the greater mineralizing effect of  $H_2SiF_6$  compared to  $MgF_2$ .

It should be noted that despite the introduction of the mineralizator the synthesized powders in their composition contain a little content of free  $MgO$ . On diffractograms it is also observed the disproportionate change of peaks intensity that correspond to forsterite and periclase. This can be related to the fact that the formation of latter one takes place at grain boundaries of forsterite with the formation of periclase layers and with the detention of forsterite crystal growth.

The obtained results allow to state that the introduction of mineralizing fluor containing additive in the system of  $MgO-SiO_2$  enables to lower the temperature of the mineral formation in the system, but its effect does not extend to a substantial reduction of  $MgO$ , ions  $F^-$  are not able to accelerate the diffusion of cations  $Mg^{2+}$  compared to  $Si^{4+}$ .

Obviously, for monophasic forsterite powder obtention there should be an extend isothermal holding at the maximum temperature. Considering this, there were obtained powders, for which the optimal parameters of synthesis are: burning temperature of 900 °C, isothermal holding for 3 h, that are confirmed by XRD.

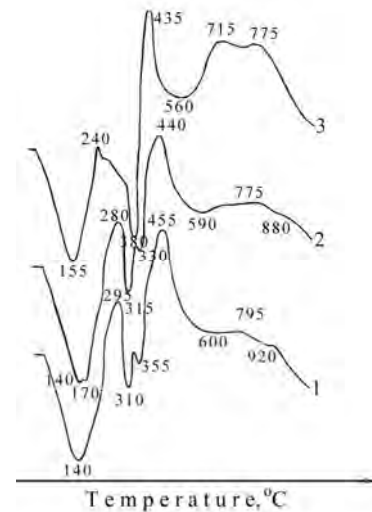


Fig. 5. DTA of xerogels:  
 1 – without mineralizers;  
 2 – with  $MgF_2$  mineralizator;  
 3 – with  $H_2SiF_6$  mineralizator

The forsterite powder synthesis scheme  $2\text{MgO}\cdot\text{SiO}_2$  by sol-gel method is as follow (Fig. 6).

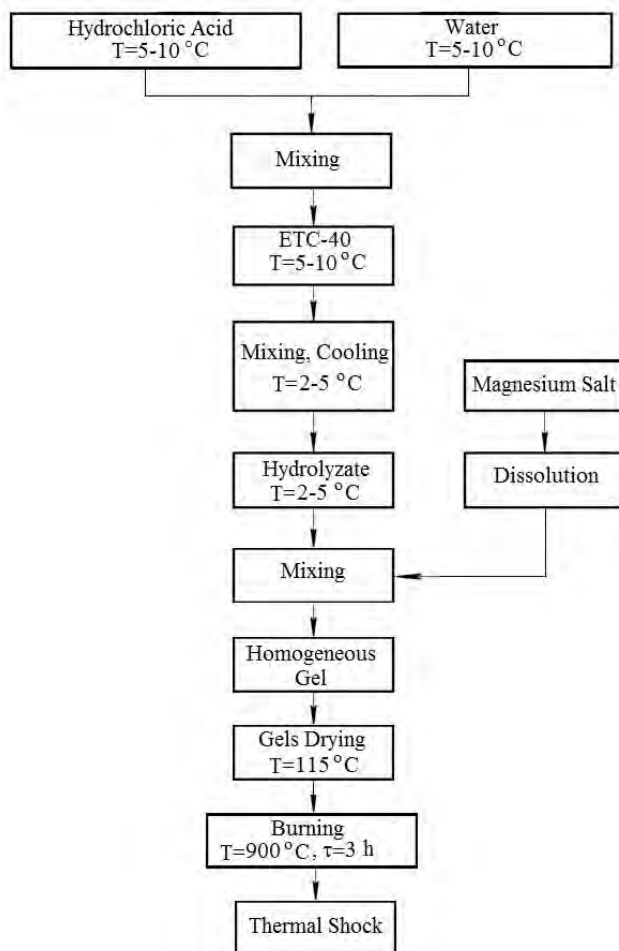


Fig. 6. The scheme of sol-gel synthesis of forsterite powder

**Conclusions.** A result of the research the technological sol-gel method conditions of the monophasic powders obtention of forsterite composition were developed. It is shown that for their production a crystalline magnesium acetate  $\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  should be used as a magnesium containing component, which speeds up the process of gelation in the system of  $\text{MgO}\text{-SiO}_2$ . It is found that xerogels after drying are X-ray amorphous. The first signs of forsterite formation are seen in powders synthesized at  $700\text{ }^\circ\text{C}$ . DTA and XRD methods confirm the expediency of using fluoride containing mineralizators of  $\text{MgF}_2$  and  $\text{H}_2\text{SiF}_6$ , which allow to reduce the temperature of the mineral formation in the system to  $100\text{ }^\circ\text{C}$ . The mineralizing effect of  $\text{F}^-$  ion, introduced into the sol composition by a liquid acid  $\text{H}_2\text{SiF}_6$  is higher compared to  $\text{MgF}_2$ .

1. Попович Н. В. Особенности кинетики процесса синтеза люминесцентных материалов золь-гель методом / Н. В. Попович, В. В. Федоров // *Стекло и керамика*. – 2000. – № 3. – С. 8–10.
2. Подденежный Е. Н. Классификация способов получения ультрадисперсных оксидных порошков (обзор) / Е. Н. Подденежный, А. А. Бойко // *Вестник ГГТУ им. П. О. Сухого*. – 2003. – № 1. – С. 21–28.
3. Mehrotra R. C. Role of metal alkoxides in molecular desing of novel oxide ceramic material by the sol-gel process / R. C. Mehrotra // *Nat. Acad. Sci. Lett.* – 1991. – Vol. 14 (4). – P. 153–160.
4. Kharaziha M. Synthesis and characterization of bioactive forsterite nanopowder / M. Kharaziha, M. H. Fathi // *Ceram. Intern.* – 2009. – Vol. 35 (6). – P. 2449–2454.
5. Аветиков В. Г. Магнезиальная электротехническая керамика / В. Г. Аветиков, Э. И. Зинько. – М.: Энергия, 1973. – 184 с.
6. Preparation of Forsterite by Pyrolysis of a Xerogel: the Effect of Water / [Park D. G., Duchamp J. C.,

Duncan T. M., Burlitch J. M.] // *Chem. Mater.* – 1994. – Vol. 6 (11). – P. 1990–1995. 7. Kozakos A. Preparation and Densification of Forsterite ( $Mg_2SiO_4$ ) by Nanocomposite Sol-Gel Processing / A. Kozakos, S. Komarneni, R. Roy // *Mater. Latt.* – 1990. – Vol. 9 (10). – P. 405–409. 8. Влияние природы исходных компонентов на синтез форстерита, полученного золь-гель методом / Н. Т. Андрианов, С. С. Стрельникова, С. М. Дягилец [и др.] // *Стекло и керамика.* – 2002. – № 6. – С. 16–19. 9. Афонина Г. А. Получение порошка форстерита методами золь-гель технологии / Г. А. Афонина, В. Г. Леонов, О. Н. Попова // *Стекло и керамика.* – 2005. – № 8. – С. 19–23. 10. Matthew B. D. Mitchell. Preparation of Forsterite ( $Mg_2SiO_4$ ) Powders Via an Aqueous Route Using Magnesium Salts and Silicon Tetrachloride ( $SiCl_4$ ) / Matthew B. D. Mitchell, David Jackson, Peter F. James // *J. of Sol-Gel Science and Technology.* – 1999. – Vol. 15 (3). – P. 211–219. 11. Takayuki Ban. Low-Temperature Crystallization of Forsterite and Orthoenstatite / Takayuki Ban, Yutaka Ohya, Yasutaka Takahashi // *J. Amer. Ceram. Soc.* – 1999. – Vol. 82 (1). – P. 22–26. 12. Волконский Б. В. Минерализаторы в цементной промышленности / Б. В. Волконский, П. Ф. Коновалов, С. Д. Макашев. – М.: Стройиздат, 1963. – 192 с. 13. Вайвад А. Я. Магнезиальные вяжущие вещества / А. Я. Вайвад. – Рига: Наука, 1971. – 315 с. 14. Семченко Г. Д. Золь-гель процесс в керамической технологии / Г. Д. Семченко – Харьков, 1997. – 144 с. 15. Гидролитическая поликонденсация этилсиликата с солями меди минеральных и органических кислот в золь-гель процессе / В. А. Свицерский, М. Г. Воронов, С. В. Клименко [и др.] // *Журнал прикладной химии.* – 2001. – Т. 74, № 12. – С. 2027–2030. 16. Вахула Я. И. Влияние величины рН и концентрации реагентов на гелеобразование магнийсиликатных коллоидных растворов / Я. И. Вахула, И. В. Луцюк, И. Д. Борищшин // *Журнал прикладной химии.* – 2008. – Т. 81. – Вып. 5. – С. 872–874.