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МОДИФІКУВАННЯ КЕРАМІЧНОГО ПОРОШКУ СИСТЕМИ $MgO–SiO_2$ ІОНАМИ Cr^{3+}, Y^{3+}, Zr^{4+}

Встановлена можливість отримання керамічних порошків форстеритового складу, модифікованих іонами Cr^{3+}, Y^{3+} та Zr^{4+}. Методом РФА встановлено фазовий склад порошків. Досліджено, що введення іонів-модифікаторів до складу гелеутворювального розчину призводить до структурних змін, які дають змогу отримати монофазний порошок із високим ступенем кристалічності. Визначено параметри кристалічної структури синтезованих порошків. Встановлено утворення твердих розчинів заміщення. Розроблено технологічні особливості синтезу модифікованих форстеритових порошків золь-гель-методом і кераміки на їхній основі.

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

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MODIFICATION OF CERAMIC POWDER OF SYSTEM $MgO–SiO_2$BY Cr^{3+}, Y^{3+}, Zr^{4+}IONS

The possibility of obtaining ceramic powders of forsterite composition modified by Cr^{3+}, Y^{3+}таZr^{4+} ions is established.The phase composition of powders was done by XRD method.It was investigated that introduction of ions-modifiers into the composition of gel-forming solution leads to structural changes permitting to get monophase powder with high crystallinity. The parameters of the crystal structure of the synthesized powders were determined. The formation of solid substitution solutions was established. Technological features of synthesis of modified forsterite powders by sol-gel method and ceramics on their basis weredesigned.

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

Formulation of the problem and its connection with important scientific goals. Nowadays inorganic materials based on complex oxides of different valence are broad in scope. In particular, they are used for catalyst, dielectric materials, ceramic superconductors, products for microelectronics, optically transparent ceramics, ceramics with fluorescent properties, bone implants.However, obtaining materials with high functional properties is possible in case of putting them at the time of powders.The problem of obtaining ultrafine powders is complicated by several factors (their high chemical activity, adsorption capacity, tendency to agglomeration) and these properties are largely dependent on the synthesis process.One of the promising methods for the synthesis of complex oxides are sol-gel method that allows to obtain ultra chemical powder of specified grain size and specific morphology [1, 2].

Progress in obtaining of modern ceramic materials of technical purposes directly related to the search for non-traditional types of raw materials and methods of activation. The most effective ways to activate the processes of ceramic materials is mechanochemistry methods and the introduction of modifiers. A number of works of leading foreign and domestic scientists of the high performance powders and functional ceramics generally achieved by introducing ions modifiers in the powder structure. This activation enables to obtain new materials with predetermined properties [3].

Analysis of recent research and publications. One of the representatives of oxide ceramic materials have great promise in the use of electricity and radio is forsterite ceramics [4]. This is due to the fact that forsterite ceramics with tightly sintered structure has a high value of electrical properties and increased coefficient of linear expansion, so it is used in vacuum technology as an insulator in contact with the metal [5].

Modifying of the structure of forsterite polyvalent metal ions extends the properties and applications of ceramics on its basis. Thus, fine powders of Mg_2SiO_4, modified by Ni^{2+}ions are used for the manufacture of ultra wideband optical amplifiers [6] Mn^{2+} - for the synthesis of red silicate phosphors [7], Eu^{2+}, Fe^{3+}, Dy^{3+}, Tb^{3+}, Eu^{3+} – for the production of phosphors [8], and powders of $Mg_2SiO_4:Cr^{3+}$is a promising environment for reconstructing of near infrared lasers [9].

The aim of work – research of phase composition, crystal structure of forsterite powders modified by Cr^{3+}, Y^{3+}, Zr^{4+} ions and properties of ceramics based on them.

Results and discussions. For forsterite powders obtaining of Mg_2SiO_4 composition alkoxide variant of sol-gel method was used which allows to obtain powder mixtures of different metal alkoxides at relatively low temperatures. According to research [10] the most effective reagent for the introduction of Mg^{2+}ions are hydrated magnesium acetate $Mg(CH_3COO)_2{\cdot}4H_2O$ (c= 0.7 mol/l) as a powder after gel drying is X-ray, and duration of gelling is the shortest. As a silica containing precursor Ethyl silicate hydrolyzate ETS-40 (nH_2O/C_2H_5O = 3,87, catalyst HCl) was selected. Compounds were added in the amount that provides a ratio of magnesium oxide and silicon equal to the stoichiometric in forsterite (MgO/SiO_2 = 2/1).

Synthesis of forsterite powder of $2MgO{\cdot}SiO_2$composition by sol-gel method was performed according to scheme shown in [11]. Herewith it was found that the optimal parameters of powder synthesis is the temperature of 900 °C with isothermal holding of 3 hours.

The definition of phase composition and crystal structure parameters of sintered complex powders of magnesium and silica oxides was performed by X-ray (XRD) and X-ray diffraction (XRD) analysis. Qualitative RFA was performed by comparing the experimental diffraction pattern and standard diffractions from International Centre of Diffraction Data (ICDD) PDF-2.

Structural parameters of crystalline frame of forsterite according to International Centre of Diffraction Data ICDD is shown in Table 1.

Table 1

Structural parameters of the crystal frame of forsterite[ICDD]

PDF	Unit cell parameters *, Å			*V*, Å
	a	*b*	*c*	
34-189	5,9817(5)	10,1978(8)	4,7553(3)	290,0
71-1080	4,7560(1)	10,2070 (1)	5,9800 (1)	290,3
71-1792	4,7535(4)	10,1943(5)	5,9807(4)	289,8
74-714	4,7534(7)	10,1902(6)	5,978(6)	289,5
76-561	4,7534(1)	10,1989(1)	5,9813(2)	289,9
78-1371	4,7550(3)	10,1960(3)	5,9809(6)	289,9
80-783	4,7533(3)	10,2063(1)	5,9841(1)	290,3
84-1402	4,7549(4)	10,1985(3)	5,9792(6)	289,9

*a, b i c – unit cell parameters of forsterite; V – the volume of an unit cell

According to X-ray analysis the powder of forsterite composition synthesized by optimal regime is monophasic and contains a crystalline phase of Mg_2SiO_4 (Fig. 1). Herewith it is seen the significant expansion of the diffraction peaks of crystalline phase indicating finely dispersion of powder (halfwidth reflexes in the range of angles 2θ 17–40 ° is 0,35–0,38 °, whereas crystalline materials is equal to 0,12–0,15 °).

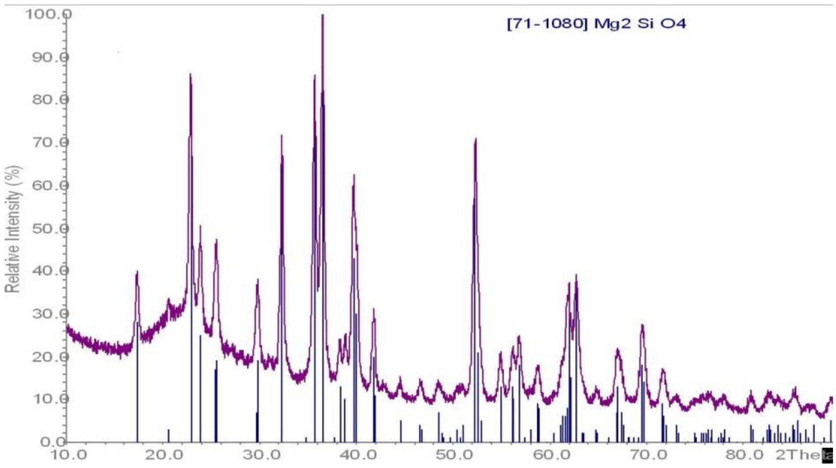


Fig. 1. Forsterite powder diffraction pattern (T=900 ºC, t=3 hours)

Using complex structural analysis programs WinCSD, it was determined the crystal structure of synthesized forsterite. Specification of unit cells parameters and atomic coordinates for crystalline phases was conducted by full profile Rietveld method using complex programs WinCSD of structural analysis.

Specified parameters and volume of the unit cell of Mg_2SiO_4 powder are almost table-valued according to International Centre of Diffraction Data ICDD and are the following (Å): a = 4.7569(4), b = 10,2175(9), c = 5.9886(5), V = 291,07(8).

The coordinates of the atoms Mg, Si and O in the structure of Mg_2SiO_4 are shown in Table 2.

Table 2

Specified coordinates and displacement parameters of atoms in the structure of forsterite

Atom	*x/a*	*y/a*	*z/a*	*B (is/eq)*	*N*
Mg 1	0	0	0	1,08(9)	4
Mg 2	0,9946(9)	0,2770(3)	¼	0,75(8)	4
Si	0,4244(6)	0,0935(3)	¼	0,57(5)	4
O 1	0,7650(12)	0,0945(7)	¼	0,8(2)	4
O 2	0,2173(13)	0,4473(8)	¼	0,1(2)	4
O 3	0,2785(9)	0,1614(5)	0,0435(7)	0,17(10)	8

One of the ways to achieve high performance functional powders and ceramics in general is the modifying of powder structure of the main composition by introducing small amounts of certain additives. This approach allows without changing the basic parameters of the developed technological regime to change significantly or reinforce the basic operational properties of powders.

For forsterite powder obtaining with higher electro properties it was done its modifying by Cr^{3+}, Y^{3+}таZr^{4+}ions in quantity 10 %(ml.) in terms of oxides [12]. The choice of ions modifiers can be explained due to the fact that Mg i $Mg^{2+}$are included into Vernadskiy isomorphic elements row (Ca, Na, Y, Sc, Mn, Sr, Ba, Pb, Fe, Mg, Zn, U (IV), Th, Zr, Cr). It can therefore be assumed that Mg^{2+}ions can form solid substitution solutions of these elements in the structure of Mg_2SiO_4 in favorable reaction conditions or specified regimes of the technological process [13]. In addition, it is known that the mechanism of powder modifying and the degree of modification depends on the input method of modifiers ions addition into the system. In this regard, modifying of the structure of the obtained powder was carried out by two different methods:

1) mechanical mixing of powder of the dried gel of base composition with Cr_2O_3, Y_2O_3andZrO_2 oxides powders.

The results of X-ray diffraction analysis of the burned powders (T = 900 ° C, τ = 3 hours) indicate that they are monophasic, and contain in its composition, besides forsterite, chrome magnesia spinel $MgCr_2O_4$ and added oxides Cr_2O_3, Y_2O_3, ZrO_2. This can be explained by the fact that modifying additives are fully dissolved in the matrix. Obviously, for their complete dissolution it is necessary to increase the temperature and the duration of isothermal holding;

2) direct introduction of water-soluble salts of $Cr(NO_3)_3{\cdot}9H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ and $ZrOCl_2{\cdot}8H_2O$ in a basic solution with subsequent gel drying by developed technology [11].

XRD method shows that powders modified by Cr^{3+}, Y^{3+}andZr^{4+}ions are single-phase and contain a crystalline phase of forsterite structure (Fig. 2).

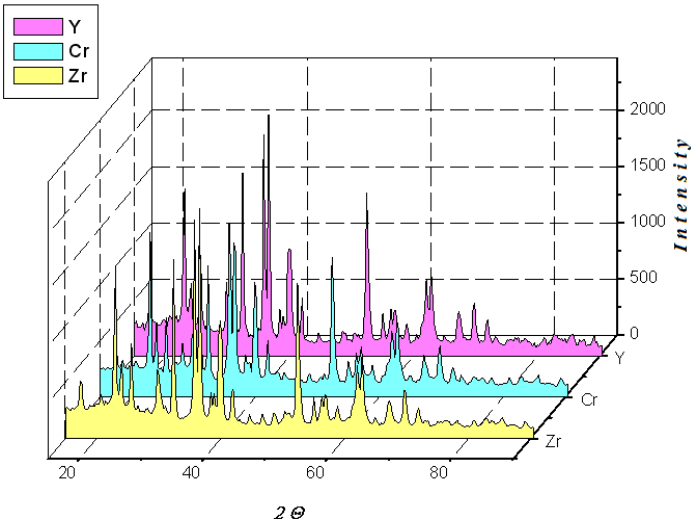


Fig. 2. Diffraction of forsterite powders modified by Cr^{3+}, Y^{3+} and Zr^{4+} ions

Analyzing the obtained parameter values of unit cells and comparing them with each other and with the published data for Mg_2SiO_4, it can be stated about partial modifier ions entering into the structure of Mg_2SiO_4 (Table 3).

Table 3

Theparametersof powdersunitcellofforsteritecomposition

The powder composition	Theparametersof anunitcell, Å			V, Å
	a	*b*	*c*	
Mg_2SiO_4	4,7569(4)	10,2175(9)	5,9886(5)	291,07(8)
Mg_2SiO_4:Cr^{3+}	4,7507(3)	10,2034(7)	5,9806(4)	289,90(6)
Mg_2SiO_4:Y^{3+}	4,7517(2)	10,2099(4)	5,9849(4)	290,35(3)
Mg_2SiO_4:Zr^{4+}	4,7550(2)	10,2146(5)	5,9847(3)	290,68(4)

Specification of the atomic place of Mg/Cr, Mg/Y та Mg/Zrshowed that ions modifiers partially substitute Mg^{2+} in the position Mg 2. As a result of calculations done through programs of structural analysis WinCSD it was found that the percentage of Chromium, Yttrium and Zirconia ions in the investigated powders is 1.18, 0.59 and 2.47 %(wt.) respectively. Herewith substitution solid solutions are formed that meet the following formulas: $Mg_{1,97}Cr_{0,03}SiO_{4+\delta}$, $Mg_{1,99}Y_{0,01}SiO_{4+\delta}$та $Mg_{1,96}Zr_{0,04}SiO_{4+\delta}$in accordance.

Particle sizes of forsterite powders were assessed by extension diffraction peaks according to Scherrer method. It was established that nanoparticles in size 35–40 nm combine in quite large agglomerates.

Research of pressing capacity of btained powders was performed on samples in the form of discs with a diameter of 16 mm and thickness of 2 mm in metal forms by specific pressure of 30, 60 and 80 MPa. As a coherent component hydrolyzate ETS-40 in an amount from 5 to 11 %(wt.) was used. It was found that the optimal quantity of ETS-40 is 9 %(wt.). This semifinished-samples have a maximum degree of compaction and strength. For ceramics semifinished products obtaining after drying at 100 °C the burning was hold at 1200 °C with isothermal holding for 6 hours.

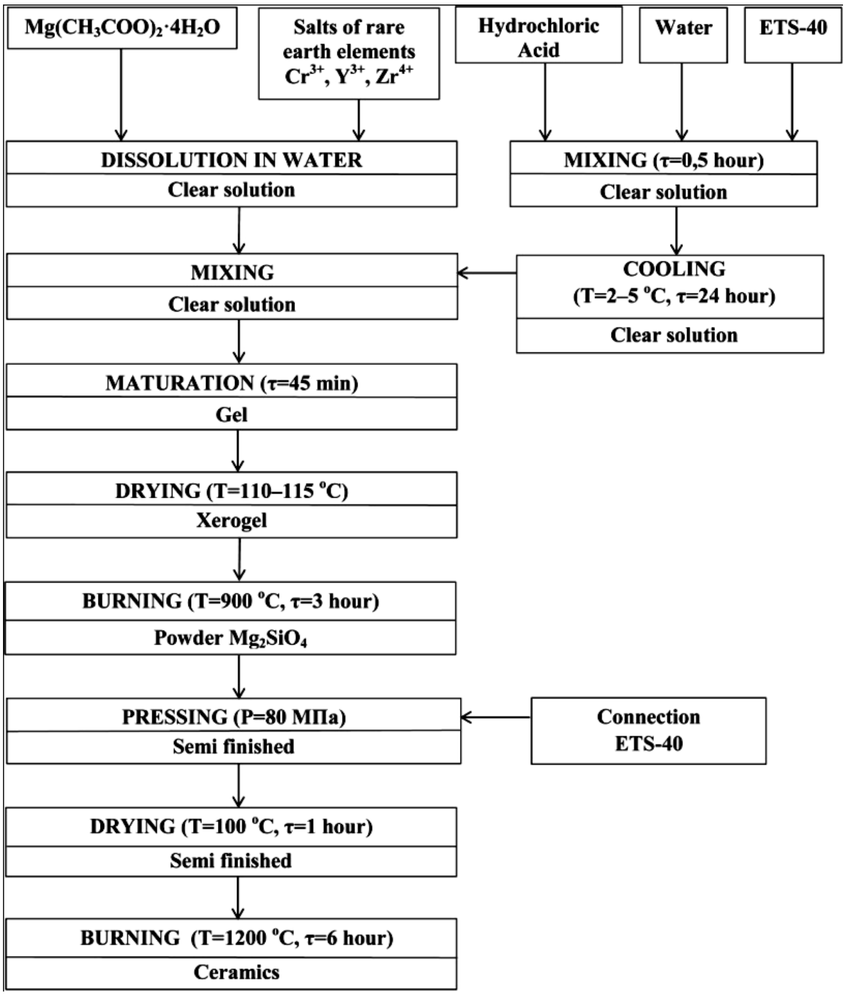
The studies (Table 4) show that water absorption of samples depends largely on the specific pressure of semi-finished samples and is equal to 4,57–0,49 %. The increase in pressure from 30 to 80 MPa leads to the decrease of water absorption in 8–8,6 times.

Table 4

Water absorption of forsterite ceramics

Sample of ceramics	Pressure, MPa		
	30	60	80
	Water absorption, %		
Mg_2SiO_4	4,33	2,56	0,54
Mg_2SiO_4:Cr^{3+}	4,19	2,23	0,49
Mg_2SiO_4:Y^{3+}	4,57	2,38	0,53
Mg_2SiO_4:Zr^{4+}	4,34	2,27	0,51

The technological scheme for obtaining modified forsterite powders by sol-gel method and ceramics on their basis is as follows.



Conclusions. As a result of research the technological scheme of forsterite powders obtaining modified by sol-gel method and ceramics on their basis was designed. The addition into the sol composition Cr^{3+}, Y^{3+}таZr^{4+}ions allows to obtain forsterite powders of modified structure. XRD and RSA methods establish the possibility of heterovalent isomorphic substitution in the structure of forsterite Mg^{2+} ions by Cr^{3+}, Y^{3+}, Zr^{4+}ions with the formation of solid solutions of $Mg_{1,97}Cr_{0,03}SiO_{4+\delta}$, $Mg_{1,99}Y_{0,01}SiO_{4+\delta}$, $Mg_{1,96}Zr_{0,04}SiO_{4+\delta}$composition. As a result, monophasic powders with high crystallinity and ceramics on their basis with predicted high electro-physical and laser characteristics were obtained.

1. Семченко Г. Д. Золь-гель процесс в керамической технологии / Г. Д. Семченко. – Харьков, 1997. – 144 с. 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. Хабас Т. А. Нанопорошки металлов в технологии керамики / Т. А. Хабас. – Томск, 2009. – 230 с. 4. KharazihaM. 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. Molten-Salt Synthesis and Characterization of Nickel-Doped Forsterite Nanocrystals / Hong-Tao Sun, Minoru Fujii, Noriko Nitta and other // J. Amer. Ceram. Soc. − 2009. – Vol. 92 (4). − P. 962–966. 7. Synthesis and Luminescence Properties of Red Phosphors: Mn^{2+} Doped $MgSiO_3$ and Mg_2SiO_4 Prepared by Sol-Gel Method /[Lin Lina, Yin Mina, Shi Chaoshub and other] // Journal of Rare Earths. − 2006. − Vol. 24 (1). − P. 104–107. 8. Synthsis and photoluminescence of Eu^{3+}-or Tb^{3+}-doped Mg_2SiO_4 nanoparticles prepared by a combined novel approach / H.Yang, J. Shi, K. W. Cheah // J. Luminesc. – 2006. –Vol.118 (2). – P. 257–264. 9. Chromium-Doped Forsterite Nanoparticle Synthesis by Flame Spray Pyrolysis / [Takao Tani, Shu Saeki, Takenobu Suzuki, Yasutake Ohishi] // J. Amer. Ceram. Soc. − 2007. – Vol. 90 (3). − P. 805–808. 10. Вахула Я. И. Влияние величины pH и концентрации реагентов на гелеобразование магнийсиликатных коллоидных растворов / Я. И. Вахула, И. В. Луцюк, И. Д. Борщишин // Прикладная химия. – 2008. – Т. 81, Вып. 5. − С. 872–874. 11. Луцюк І. В. Технологічні особливості синтезу порошків форстеритового складу / І. В. Луцюк, Я. І. Вахула // Вісник Національного університету “Львівська політехніка”. – 2016. − № 841 : Хімія, технологія речовин та їх застосування. – С. 66–71. 12. Synthesisandcharacterizationof Cr^{3+}, Y^{3+} and Zr^{4+}activatedforsteritenanoceramics / I. Karbovnyk, I. Borshchyshyn, Ya. Vakhula and others // Sensor electronics microsystem technologies: 4-th International Scientific and Technical Conference. – Odessa, 2010. – P. 263. 13. Макаров Е. С. Изоморфизм атомов в кристаллах / Е. С. Макаров. – М. : Атомиздат, 1973. − 288 с.