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LOW-TEMPERATURE FORMATION OF APATITE STRUCTURE OF NEODYMIUM SILICATE IN SILICA MATRIX

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At present silicates of one of the rare earth elements, such as neodymium, are used in various fields of technology as materials or components for lasers, solid state fuel cells, ceramics and others because of their optical, electrical, chemical and mechanical properties. Among them, $Nd_{9.33}Si_6O_{26}$ with apatite type structure occupies a significant place because of its electrical properties, as ionic conductor. In many cases, neodymium silicates are obtained by high-temperature synthesis, above 1400 °C. In our work the formation of $Nd_{9.33}Si_6O_{26}$ in silica matrix is shown at lower temperatures. By XRD method phase transformations in composites neodymium oxide - fumed silica with various molar ratios of components in the range of 1:1 to 1:20 were studied. With involvement of elemental analysis and electrical measurements, the formation of neodymium silicate with an apatite type structure was found in all the samples starting at the temperature of 920 °C. Formation of neodymium mono- or disilicate (Nd_2SiO_5 or $Nd_2Si_2O_7$) is observed only at temperatures around 1400 °C with a stoichiometric ratio of neodymium and silicon oxides (1:1 or 1:2). In our opinion, $Nd_{9.33}Si_6O_{26}$ is an intermediate phase in the formation of other neodymium silicates in such composites. As the X-ray and elemental analysis showed, the structure of $Nd_{9.33}Si_6O_{26}$ differs from perfect by larger values of the parameters of hexagonal unit cell and much smaller factor of site occupation of 4f neodymium atoms. The composite obtained by annealing of oxides Nd_2O_3 and fumed SiO_2 with a ratio of 1:20 at 1050 °C for 4 hours has an ionic conductivity on oxygen with specific conductivity value of 10^{-3}–10^{-4} $Ohm^{-1}cm^{-1}$ in the temperature up to 200 °C as indicated by the linearity of this dependence. The composite $Nd_{9.33}Si_6O_{26}$ – SiO_2 with ratio of initial oxides 1:20 also exhibits photoluminescent properties due to the multiband absorption spectrum in the UV and visible region in ranges about 200, 600, 800 nm.

***Keywords**: neodymium silicate, apatite structure, ionic conductivity, fluorescent properties, XRD and elemental analysis*

INTRODUCTION

At present silicates of rare earth elements are used in various fields of technology as materials or components for lasers, solid state fuel cells, ceramics and others because of their optical, electrical, chemical, and mechanical properties. Among them, neodymium silicates occupy a significant place. There are silicates – Nd_2SiO_5, $Nd_2Si_2O_7$, $Nd_{9.33}Si_6O_{26}$ and their solid solutions with other elements instead of Nd and Si [1–5].

According to the experimental and theoretically predicted phase diagrams of the system Nd_2O_3–SiO_2, three compounds of above neodymium silicates, their mixtures with Nd_2O_3 and SiO_2 are present [5–8]. These neodymium silicates are formed at ratio of Nd_2O_3:SiO_2 as 1:1 (Nd_2SiO_5), 7:9 ($Nd_{9.33}Si_6O_{26}$), 1:2 ($Nd_2Si_2O_7$) and coexist with Nd_2O_3 and SiO_2 when other ratios. Temperature scale of the phase diagrams denotes from about 1400 °C due to the perfect structure formation of the silicates under high-temperature synthesis. But the temperature can be reduced by using modern methods of synthesis with suitable precursors, such as different modifications of sol-gel synthesis, thereby good miscibility of the components and homogeneity of reaction mixture are achieved [9–12]. In our previous research [13–16], concerning to phase transformations in the composites based on rare earth oxides and fumed alumina and silica, neodymium silicate was detected with apatite type structure at nontypical ratio of Nd_2O_3 and SiO_2 as 1:16 and annealing temperature of 1050 °C. It is known that silicate $Nd_{9.33}Si_6O_{26}$ has ionic conductivity on oxygen, and neodymium compounds are used in optics

[17–20]. Therefore, composites based on fumed silica containing silicate $Nd_{9.33}Si_6O_{26}$ may be of interest in terms of electrical and optical properties. In this work phase transformations in composites of Nd_2O_3 and fumed SiO_2 with their different ratios and temperatures of treatment up to 1400 °C have been studied.

EXPERIMENTAL

As start reagents a fumed silica with specific surface area of 300 m^2/g (Kalush experimental plant of Chuiko Institute of Surface Chemistry) and neodymium oxide (RETC 6-09-3948-87) were used. Molar ratio of Nd_2O_3 and SiO_2 changed from 1:1 to 1:20. Characteristics of the composites are presented in Table 1. Initial mixtures were prepared by grinding of oxides in an agate mortar until to homogeneous state. The samples were annealed in a muffle furnace (SNOL-1.8, USSR) in air at 1050 °C for 2–4 h and heated in the furnace of a derivatograph Q-1500D (firm MOM, Hungary) to 1400 °C.

XRD patterns of the samples were obtained at a DRON-4-07 diffractometer (Firm "Burevestnik", Russia) with filtered CuK_α radiation in geometry of Bregg-Brentano in 2θ range of 10–80°. Phase identification was performed using the database of JCPDS. Rietveld refinement of structure parameters of the samples was carried out with FullProf Suite software. Particle morphology was studied with a scanning electron microscopy instrument MIRA3 LMU, TESCAN with a resolution of 1 nm. Energy-dispersive spectroscopic chemical analysis was carried out on an attachment to SEM – Oxford X-MAX (Great Britain), 80 mm^2 with a uncertainty of ±1 %. Conductivity was measured by a two-contact method with a frequency of 0.1, 1, 10 kHz by means of an E7-14 immitance measuring instrument in the temperature interval 20–200 °C. Complex conductivity was investigated by means of an impedance spectrometer Solartron SI 1260 in the frequency range of 10^{-1} to 10^6 Hz. Absorption spectra were recorded on a spectrophotometer Specord M40 in the wavelength range of ultraviolet and visible light from 200 to 900 nm. Fluorescence spectra were recorded on a fluorescent spectrometer LS-55, Perkin Elmer (USA) under excitation with light of the wavelength of 240 nm.

Table 1. Characteristics of composites

Sample No	Molar ratio Nd_2O_3:SiO_2	Content of SiO_2 mol. %	Expected compound according to phase diagram
1	1:1	50	Nd_2SiO_5
2	7:9	56	$Nd_{9.33}Si_6O_{26}$
3	2:3	60	$Nd_{9.33}Si_6O_{26}$
4	1:2	67	$Nd_2Si_2O_7$
5	1:10	91	$Nd_2Si_2O_7 + SiO_2$
6	1:20	95.3	$Nd_2Si_2O_7 + SiO_2$

RESULTS AND DISCUSSION

Preliminary X-ray diffraction data on the composite 6 have shown that formation of hexagonal $Nd_{9.33}Si_6O_{26}$ occurs since the temperature of 920 °C and continues at least until 1050 °C. Diffraction patterns of the samples annealed at 1050 °C for 2 h are presented in Fig. 1. It is seen that in all cases $Nd_{9.33}Si_6O_{26}$ is observed. Amount of Nd_2O_3 decreases with increasing of silica content and annealing time as it is clear from Figs. 1, 2.

Annealing at this temperature leads to compaction of the samples without silica crystallization. At the same time, in the presence of some other oxides fumed silica is capable to crystallize to cristobalite form [21–23].

Further heat treatment of the samples was performed using a furnace derivatograph upon to 1400 °C with the simultaneous recording of the weight loss curve (TG), the differential weight loss curve (DTG) and the differential thermal analysis curve (DTA). The thermographic curves of all samples showed a similar appearance and they are presented in Fig. 3 for the sample 6 only. Weight loss and respective thermal effects, observed up to ~800 °C, are related to decomposition of neodymium hydroxide, which is a source of neodymium oxide in the composites. In high temperature range of 800–1400 °C no weight loss or visible thermal effect is observed. DTA curve gradually increases with a slight change in slope near 1200 °C.

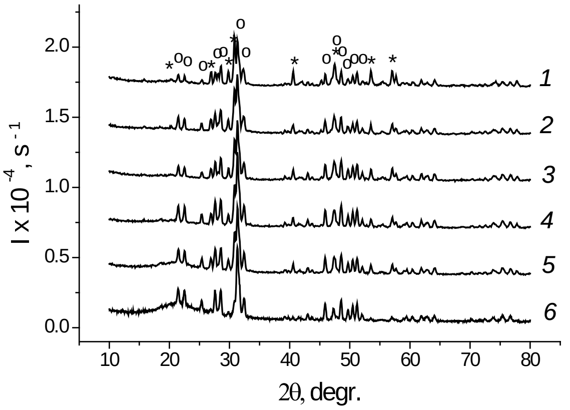

Fig. 1. XRD patterns of the samples annealed at 1050 °C, 2 h. Symbol designation: o – $Nd_{9.33}Si_6O_{26}$, * – Nd_2O_3

XRD analysis of the samples heated in derivatograph furnace has shown that only apatite type structure of $Nd_{9.33}Si_6O_{26}$ is saved in the sample 2 with a stoichiometric ratio of components to form such a silicate. In the samples 1 and 3–6, phases corresponding to the phase diagram begin to crystallize. There are Nd_2SiO_5 for sample 1, $Nd_{9.33}Si_6O_{26}$ with SiO_2 (cristobalite) for sample 3, and $Nd_2Si_2O_7$ with SiO_2 (cristobalite) for samples 4–6. Fig. 4 illustrates these transformations.

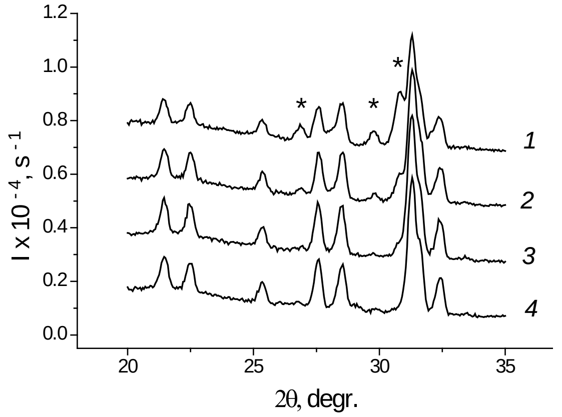

Fig. 2. Angular interval of XRD patterns with the main $Nd_{9.33}Si_6O_{26}$ peaks of sample 6, annealed at 1050 °C for 1 (*1*), 2 (*2*), 3 (*3*), 4 (*4*) h. Symbol designation: * – Nd_2O_3

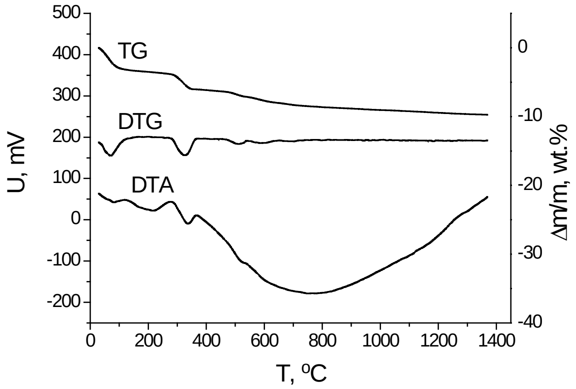

Fig. 3. Derivatogram of initial composite 6

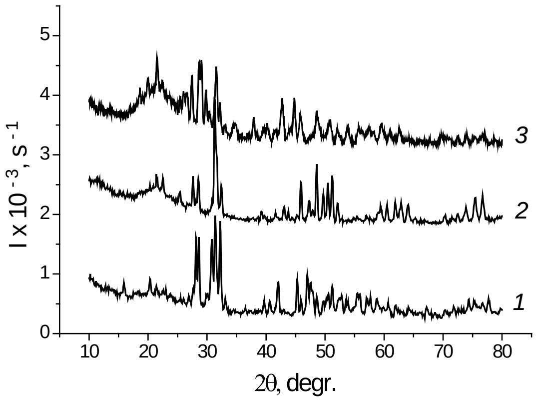

Fig. 4. XRD patterns of the samples: 1 (*1*), 2 (*2*), 6 (*3*) heated to 1400 °C. Main phases: Nd_2SiO_5 (*1*), $Nd_{9.33}Si_6O_{26}$ (*2*), $Nd_2Si_2O_7$ (*3*)

Thus, phase $Nd_{9.33}Si_6O_{26}$ is an intermediate in the synthesis of neodymium mono- and disilicate in the composites with the ratio of Nd_2O_3 and fumed SiO_2 differing from 7:9, which is required for formation of silicate $Nd_{9.33}Si_6O_{26}$. Based on the change in the slope of the DTA curve, it can be assumed that the neodymium silicate phase with the apatite type structure exists in such systems up to temperatures of about 1200 °C.

Visually diffraction pattern of $Nd_{9.33}Si_6O_{26}$ in all samples annealed at 1050 °C and sample 2 heated to 1400 °C, is the same, namely positions of the diffraction peaks and their relative intensities.

To specify the structure parameters of the $Nd_{9.33}Si_6O_{26}$ phase in the composites, Rietveld profile analysis was applied. The program Full Prof was exploited to the refinement of diffraction patterns of the sample 6 annealed at 1050 °C for 4 h and sample 2 heated to 1400 °C. The theoretical curves are calculated based on the parameters of the structure of $Nd_{9.33}Si_6O_{26}$, taken from the NIST database for single crystal of the silicate [24]. The results of refinement are shown in Fig. 5, as Rietveld refinement plot, for the sample 6 only. Main original and refined parameters, such as the unit cell parameters and site occupation factor (SOF) for 4*f* positions of neodymium atoms, are presented in Table 2.

It can be seen that the crystalline structure of the silicate in the composites studied is far from perfect. The parameters of its hexagonal cell are larger, and the site occupation factor of position 4*f* by Nd atoms is much smaller than that for a single crystal.

Investigation of the morphology of particles in composite 6 using scanning electron microscopy has shown the formation of dense aggregates of particles of several μm in length with a particle size of 0.1–0.3 μm in a medium of less aggregated particles with a size of tens of nm (Fig. 6). According to elemental analysis of such regions in more denser aggregates, the atomic ratio of Nd and Si is close to the characteristic ratio for $Nd_{9.33}Si_6O_{26}$, in a less dense medium, Nd is practically absent (Fig. 7, Table 3).

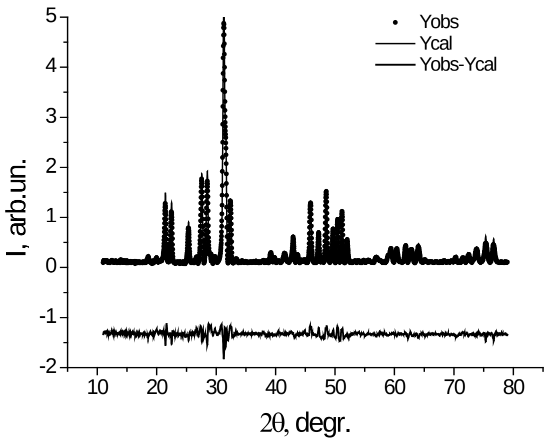

Fig. 5. Rietveld refinement plot of the sample 6 annealed at 1050 °C for 4 h

Table 2. Results of Rietveld refinement of the samples

Sample, containing $Nd_{9.33}Si_6O_{26}$	*a*, nm	*c*, nm	SOF of 4*f* Nd
6, annealed at 1050 °C for 4 h	0.95705	0.70289	0.536
2, heated to 1400 °C	0.95689	0.70213	0.549
single crystal	0.95556	0.70192	0.854

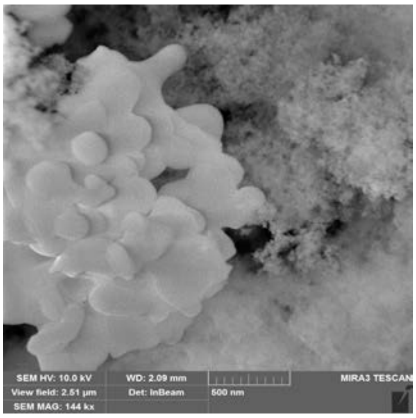

Fig. 6. SEM image of composite 6 annealed at 1050 °C for 4 h

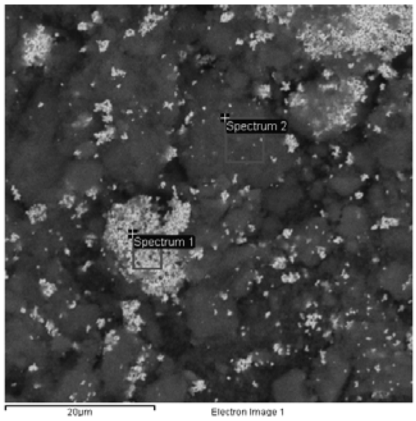

Fig. 7. Part of SEM image for chemical analysis of composite 6 annealed at 1050 °C for 4 h

To confirm the formation of neodymium silicate with an apatite structure in composites based on neodymium oxide and fumed silica at temperatures above 920 °C, the temperature dependence of the electrical conductivity of composite 6 annealed at 1050 °C for 4 h, mixture of sample 2 heated to 1400 °C, and silica with their ratio as in composite 6, was measured. Cooling curves are shown in Fig. 8. It is seen that curves cooling for both samples have linear character. This indicates that these samples have ionic conductivity, known as oxygen conductivity.

Table 3. Results of energy-dispersive spectroscopic chemical analysis of the composite 6 annealed at 1050 °C for 4 h

Element	O	Si	Nd
Spectrum 1	62.23	15.62	22.15
Spectrum 2	68.60	31.09	0.32
Mean	65.42	23.35	11.23
Std. deviation	4.50	10.94	15.44
Max	68.60	31.09	22.15
Min	62.23	15.62	0.32

All results in atomic %

Low values of conductivity about 10^{-3}–10^{-4} $Ohm^{-1}cm^{-1}$, apparently, are due to low degree of perfect silicate structure and also to sufficiently low temperature of heating. It should be noted that the slope of the conductivity curves of these samples is different. The higher slope corresponds to the sample containing $Nd_{9.33}Si_6O_{26}$ obtained as a result of heating of composite 2 at 1400 °C. It correlates with the structural parameters of the silicate in this composite.

Composites consisting of $Nd_{9.33}Si_6O_{26}$ and a silica matrix were tested for fluorescence properties. Fig. 9 *a* shows the absorption spectrum of the composite 6 annealed at 1050 °C. It can be seen a number of intense bands in the wavelength range 200, 600, and 800 nm. When excited at the wavelength of 240 nm, close to that of the largest absorption by the sample, fluorescence is observed at the wavelength of 395 nm (Fig. 9 *b*). Consequently, the presence of neodymium silicate with the apatite type structure in the composites under consideration can give them fluorescent properties.

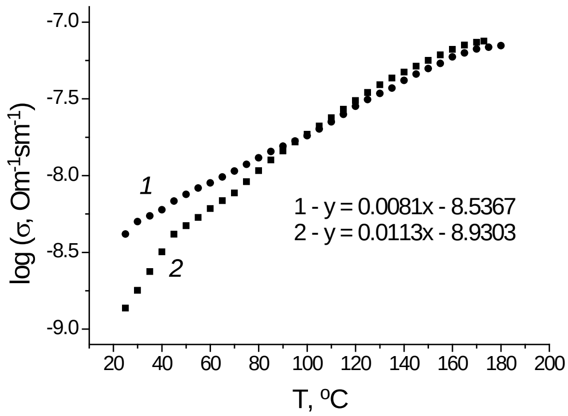

Fig. 8. Logarithm of conductivity of composite 6 annealed at 1050 °C (*1*), mixture of composite 2 heated to 1400 °C, and SiO_2 with their ratio as in composite 6 (*2*)

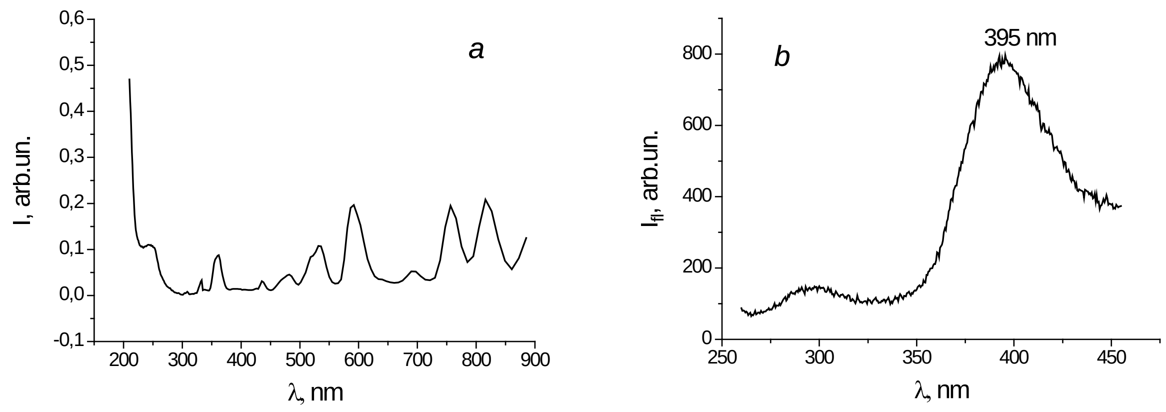

Fig. 9. UV-Vis absorption spectrum (*a*) and fluorescence spectrum at λ_{ex} = 240 nm (*b*) of the sample 6 annealed at 1050 °C for 4 h

CONCLUSION

Thus, when using XRD and elemental analysis data, electrical conductivity measurements, it has been found that in the composites based on fumed silica and neodymium oxide, the neodymium silicate with apatite type structure $Nd_{9.33}Si_6O_{26}$ is formed starting at 920 °C for the ratios of initial Nd_2O_3 and SiO_2 in the range 1:1–1:20. It appears intermediate for composites with a ratio of oxides other than 7:9 and presumably exists up to temperatures of about 1200 °C. The structure

of $Nd_{9.33}Si_6O_{26}$ differs from perfect by larger values of the parameters of the unit cell and a smaller factor of site occupation of 4*f* neodymium atoms. The composite obtained by annealing of oxide Nd_2O_3 and fumed SiO_2 with the ratio of 1:20 at 1050 °C has oxygen ionic conductivity with specific value of 10^{-3}–10^{-4} $Ohm^{-1}cm^{-1}$ in the temperature range up to 200 °C. Such a composite also exhibits photoluminescent properties due to the multiband absorption spectrum in the UV and visible regions.

Низькотемпературне формування силікату неодиму зі структурою апатиту в кремнеземній матриці

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Досліджено фазові перетворення в композитах оксид неодиму – пірогенний кремнезем з різним молярним співвідношенням компонентів в межах від 1:1 до 1:20. Показано, що формування силікату неодиму $Nd_{9.33}Si_6O_{26}$ зі структурою апатиту відбувається у всіх композитах за температури вище 900 °C. Утворення моно- або дисилікату неодиму спостерігається лише при температурах, близьких до 1400 °C, за умови відповідних стехіометричних співвідношень оксидів неодиму і кремнію. Виміри електричної провідності композиту із співвідношенням оксидів 1:20, відпаленого при 1050 °C протягом 4 год (іонна провідність за киснем), узгоджуються з даними рентгенофазового та елементного аналізу. Показано, що даний композит має флуоресцентні властивості.

***Ключові слова**: силікат неодиму, апатитна структура, іонна провідність, флуоресцентні властивості, рентгенофазовий та елементний аналіз*

Низкотемпературное формирование силиката неодима со структурой апатита в кремнеземной матрице

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Исследованы фазовые превращения в композитах оксид неодима – пирогенный кремнезем с различным молярным соотношением компонентов в диапазоне от 1:1 до 1:20. Было показано, что образование силиката неодима $Nd_{9.33}Si_6O_{26}$ со структурой апатита происходит во всех композитах при температуре выше 900 °C. Формирование моно- или дисиликата неодима наблюдается только при температурах вблизи 1400 °C при соответствующем стехиометрическом соотношении оксидов неодима и кремния. Измерения электрической проводимости композита с соотношением оксидов 1:20, отожженного при 1050 °C (ионная проводимость по кислороду), согласуются с данным рентгенофазового и элементного анализа. Показано, что этот композит имеет флуоресцентные свойства.

***Ключевые слова**: силикат неодима, апатитовая структура, ионная проводимость, флуоресцентные свойства, рентгенофазовый и элементный анализ*

REFERENCES

1. Jiang C., Wu S., Ma Q., Mei Y. Synthesis and microwave dielectric properties of Nd_2SiO_5 ceramics. *J. Alloys Compd*. 2012. **544**: 141.
2. Ke S., Wang Y., Pan Z. Synthesis of $Nd_2Si_2O_7$ ceramic pigment with LiCl as a mineralizer and its color property. *Dyes and Pigments*. 2014. **108**: 98.
3. Ke S., Wang Y., Pan Z. Effects of precipitant and surfactant on co-precipitation synthesis of $Nd_2Si_2O_7$ ceramic pigment. *Dyes and Pigments*. 2015. **118:** 145.
4. Takeda N., Itagaki Y., Aono H., Sadaoka Y. Preparation and characterization of $Ln_{9.33+x/3}Si_{6-x}Al_xO_{26}$ (Ln=La, Nd and Sm) with apatite-type structure and its application to a potentiometric O_2 gas sensor. *Sens. Actuators, B*. 2006. **115**(1): 455.
5. Kobayashi K., Sakka Y. Rudimental research progress of rare-earth silicate oxyapatites: their dentification as a new compound until discovery of their oxygen ion conductivity. *J. Ceram. Soc. Japan*. 2014. **122**(8): 649.
6. Miller R.O., Rase D.E. Phase equilibrium in the system Nd_2O_3–SiO_2. *J. Am. Ceram. Soc.* 1964. **47**(12): 653.
7. Masubuchi Y., Higuchi M., Kodaira K. Reinvestigation of phase relations around the oxyapatite phase in the Nd_2O_3–SiO_2 system. *J. Cryst. Growth*. 2003. **247**(1–2): 207.
8. Saal J.E., Shin D., Stevenson A.J., Messing G.L., Liu Z.K. First-principles thermochemistry and thermodynamic modeling of the Al_2O_3–Nd_2O_3–SiO_2–Y_2O_3 pseudoquaternary system. *J. Am. Ceram. Soc*. 2010. **93**(12): 4158.
9. Devi S., Kumar S., Duhan S. Formation and structural characterization of nanocrystalline neodymium silicates prepared by the chemical process. *International Journal of Electronics Engineering*. 2010. **2**(1): 205.
10. Li H., Baikie T., Pramana S.S., Shin J.F., Keenan P.J., Slater P.R., Brink F., Hester J., An T., White T.J. Hydrothermal synthesis, structure investigation, and oxide ion conductivity of mixed Si/Ge-based apatite-type phases. *Inorg. Chem*. 2014. **53**(10): 4803.
11. Borisova E.V., Ignatov A.V., Get'man E.I., Loboda S. N., Ardanova L.I., Pasechnik L.V., Ponurovsky V.S. Sol-gel synthesis, X-ray diffraction studies, and electric conductivity of sodium europium silicate. *Hindawi Publishing Corporation Journal of Chemistry*. 2013. **2013(**Article ID 251349): 6 pages.
12. Hailea S.M., Wuensch B.J. X-ray diffraction study of $K_3NdSi_7O_{17}$: a new framework silicate with a linear Si-O-Si bond. *Acta Crystallogr., Sect. B: Struct. Sci*. 2000. **56**(5): 773.
13. Oranska O.I., Gornikov Yu.I. Phase transformations in composites $(SiO_2)_n(Al_2O_3)_{1-n}$ / Nd_2O_3. *Physical Phenomena in Solids*: Proc. 12^{th} Intern. Scientific Conf. (Kharkiv, 2015). P.115. [In Russian].
14. Oranska O.I., Gornikov Yu.I. Solid-state reactions in composites Nd_2O_3 - fumed silica with different content of Nd_2O_3. *Chem. Phys. Technol. of Surface*: Proc. All Ukr. Conf. with Intern. Part. (Kyiv, 2016). P.129.
15. Oranska O.I., Gornikov Yu.I. Phase transformations in nanocomposites based on fumed silica, alumina and rare earth oxides Ln_2O_3 (Ln = Nd, Gd). *Him. Fiz. Technol. Poverhni*. 2017. **7**(2): 155. [In Ukrainian].
16. Oranska O.I., Brichka A.V., Gornikov Yu.I. Structure and optical properties of Nd_2O_3-, $Nd_{9.33}Si_6O_{26}$-fumed silica composites. In: *Chem. Phys. Technol. of Surface*: Proc. All Ukr. Conf. with Intern. Part. (Kyiv, 2017). P.115.
17. Nakajima T., Nishio K., Ishigaki T., Tsuchiya T. Preparation and electrical properties of $Ln_x(SiO_4)_6O_{(1.5x-12)}$ (Ln: Nd, La) with apatite structure. *J. Sol-Gel Sci. Technol.* 2005. **33**(1): 107.
18. Kobayashi K., Sakka Y. Research progress in nondoped lanthanoid silicate oxyapatites as new oxygen-ion conductors. *J. Ceram. Soc. Jpn.* 2014. **122**(11): 921.
19. Liu H., Liao L., Zhang Y., Zhou T., Guo Q., Li L., Mei L. Structure refinement and luminescence properties of a novel apatite-type compound $Mn_2Gd_8(SiO_4)_6O_2$. *Dyes and Pigments*. 2017. **140**: 87.

20. Isaev V.A., Kopytov G.F., Lebedev A.V., Plautskiy P.G. Structure and spectral luminescent properties of the silicates of rare earths with apatite structure. *Scientific Journal of KubSAU.* 2012. **78**(04): 1. [In Russian].
21. Boratyrev V.M., Borysenko L.I., Oranska O.I., Galaburda M.V. Nanocomposites M_XO_Y / SiO_2 based on fumed silica and acetates Ni, Mn, Cu, Zn, Mg. *Chem. Phys. Technol. of Surface*. 2009. **15**: 294. [In Russian].
22. Sulim I.Y., Borysenko M.V., Korduban O.M., Gun'ko V.M. Influence of silica morphology on characteristics of grafted nanozirconia. *Appl. Surf. Sci*. 2009. **255**(17): 7818.
23. Kulik K.S., Borysenko M.V. Synthesis and properties of nanocomposites CeO_2 / SiO_2. *Chem. Phys. Technol. of Surface*. 2009. **15**: 303. [In Russian].
24. Okudera H., Yoshiasa A., Masubuchi Y., Kikkawa S. Determinations of crystallographic space group and atomic arrangements in oxide-ion-conducting $Nd_{9.33}(SiO_4)_6O_2$. *Crystalline Materials.* 2004. **219**(1): 27.

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