

SOL-GEL PROCESSED $\text{SiO}_2\text{-Al}_2\text{O}_3$ XEROGELS: SYNTHESIS AND LUMINESCENT PROPERTIES

S. S. Smola¹, Ye. N. Fadieiev¹, M. Yu. Rusakova², N. P. Efryushina¹, N. V. Rusakova^{1*}

¹ A. V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine; 86 Lyust-dorfskaya doroga, Odessa 65080, Ukraine

² I. I. Mechnikov Odessa National University; 2 Dvoryanskaya str., Odessa 65082, Ukraine

*e-mail: natavrusakova@gmail.com

$\text{SiO}_2\text{-Al}_2\text{O}_3$ xerogels with various Si : Al ratios were synthesized via sol-gel method (two kinds of synthetic procedures were used) and characterized by means of elemental analysis, XRD, thermogravimetry and IR spectroscopy. No losses of precursors were found during the synthesis and the introduced components are quantitatively transferred from the initial mixture to the composition of the formed samples. The position of the luminescence band in the 300–500 nm region depends on the wavelength of the exciting light, time of gel maturation and the drying temperature, which is the manifestation of the influence of the structure of units in xerogels on the luminescent properties.

Key words: sol-gel method, silica, alumina, photoluminescence.

INTRODUCTION. Silicon oxide is widely used in the production of materials by the sol-gel method. Besides silica one of the most commonly used carriers as a basis for the creation of lasers, optical waveguides, chemical sensors and molecular thermometers is aluminum oxide [1–3]. The sol-gel method for the synthesis of materials based on it with controlled nanoarchitecture and ease of composition adjustment has a number of advantages. It is the ability to control the properties of materials in the process of their synthesis, including the specific surface area and porosity, changing the pH, type of precursor, temperature, solvent. The resulting materials are characterized by a

specific surface area less than 300 m²/g and a wide pore size distribution with a maximum in the range of 2–20 nm. However, it is hard to obtain alumina hybrid materials with encapsulated organic molecules and metal complexes by the classical sol-gel method, as a wide number of the organic components in hybrid materials begin to break down at a temperature > 250 °C [4, 5].

Therefore, hybrid materials obtained by a combination of several inorganic matrices - oxides of silicon, aluminum, titanium, etc. are often used (“mixed matrices”) [6–9]. Depending on the mixing sequence of the components, both microheterogeneous and homogeneous

samples can be obtained. The formation of homogeneous materials is achieved by simultaneous mixing of all precursors with the formation of interpenetrating networks of two or more inorganic matrices, including the formation of bonds of the Si-O-Al (Si-O-Ti) type [10–12]. In such systems, phase separation processes do not occur, but this is quite difficult to achieve due to the limited solubility of some precursors in the sol-gel process media or due to the increased tendency of one of the precursors to premature polycondensation.

In this regard, the aim of this work was, first, to obtain mixed matrices of silica-alumina, by hydrolysis of their alkoxides mixed in different ratios. Second, the investigation of luminescent properties in relation to their composition and structure for understanding the possibility of anchoring luminescent lanthanide complexes and obtaining highly luminescent lanthanide-containing hybrid materials

EXPERIMENT AND DISCUSSION OF THE RESULTS. All reagents and solvents purchased from commercial suppliers had the analytical-grade and used without further purification.

Elemental analysis for silicon and aluminum content was carried out by atomic absorption on a Shimadzu A7000 spectrometer using flame atomization. Samples were fused in platinum cups with a mixture of tetraborate-lithium fluoride at 950°C, the fusion product was dissolved in a mixture of hydrochloric and tartaric acids.

IR spectra (4000–400 cm^{-1}) were registered on a Perkin-Elmer Frontier FTIR spectrometer in KBr pellets.

X-ray diffraction analysis was performed on a Supernova diffractometer (Agilent Technologies). Diffraction spectra were obtained in filtered copper radiation ($\text{Cu K}\alpha$, anode

voltage 30 kV, current strength 20 mA, initial slits 2.4 mm, slit on the detector 0.1 mm). Diffraction patterns were recorded in a discrete mode: scanning step 0.05°, exposure time at each point 4 s. The range of angles of the diffraction spectra (2θ) was 10–90°.

Thermogravimetric curves (DTA, DTG, TG) were recorded on a Q-1500D thermogravimetric analyzing system (Paulik-Paulik-Erdey) in air. Samples weighing about 400 mg were heated at a rate 5 deg/min in the temperature range 20–600°C, calcinated aluminum oxide served as a standard.

The luminescence excitation and emission spectra were recorded on a Fluorolog FL 3–22 spectrofluorimeter, Horiba Jobin Yvon (Xe lamp 450 W), equipped for measurements both at room temperature and at 77 K (PMT R928P for the visible region).

Al_2O_3 xerogels were obtained by two methods. The first was the mixing of tetraethoxysilane and aluminum isopropoxide in an ethanol-water-ammonia system. The samples were kept for 24 hours at room temperature, dried for two weeks, with a gradual increase in temperature to 120°C. Materials with a molar fraction of aluminum from 0 to 20% were obtained by this method (further increase in the proportion of aluminum could not be achieved).

The second approach is based on the use of liquid aluminum alkoxide (sec-butoxide). A mixture of silicon and aluminum alkoxides in a certain ratio was placed in a desiccator containing 25% ammonia solution, and left for two weeks at $T = 20\text{--}25^\circ\text{C}$. As a result of diffusion of water and ammonia vapors into the liquid, hydrolysis and polycondensation of alkoxides occur, which is significantly slowed down compared to the classi-

cal sol-gel process. The samples were dried at 120°C. It is worth noting that with the use of this approach samples with Al content higher than 20% mol can be obtained, but they are not considered in this work. Samples with $\mu(\text{Si}) = 100\%$ (or $\mu(\text{Al}) = 0\%$) and $\mu(\text{Al}) = 100\%$ were also obtained for comparison from pure tetraethoxysilane and sec-butoxide aluminum, respectively.

The concentration of silicon and aluminum was determined by atomic absorption spectroscopy. As can be seen from table 1, the mass fraction of aluminum is 0–5.4 mass %. The proportion of silicon decreases from 41.6 to 32.7% with increasing aluminum concentration. The table also shows the calculated pro-

portions of aluminum and silicon, which are close to the stoichiometric ratio used during the synthesis. It can be assumed that during the synthesis there are no losses of precursors and the introduced components are quantitatively transferred from the initial mixture to the composition of the formed samples. Based on the conditional formula of materials $x\text{SiO}_2 \cdot y\text{Al}_2\text{O}_3 \cdot z\text{H}_2\text{O}$, the amount of water was calculated. An increase in the concentration of alumina leads to an increase in the amount of water in the materials from 10.8 to 14.6%, which is due to its increased affinity for water. The water content data obtained by elemental analysis agree well with the thermogravimetry data.

Table 1

Elemental and thermogravimetric analyzes data of xerogels

Calculated		Found					
Mole fractions (μ), %		Mole fractions (μ), %		Mass fractions (ω), %		Mass fractions ($\omega \text{H}_2\text{O}$), %	
						Elemental analysis*	Thermo- gravimetry
Al	Si	Al	Si	Al	Si	H ₂ O	H ₂ O
0,0	100,0	0,0	100,0	0,0	41,6	10,8	11,2
2,5	97,5	2,3	97,7	0,9	39,8	12,2	12,5
5,0	95,0	4,8	95,2	1,8	38,4	12,5	12,7
7,5	92,5	7,2	92,8	2,8	36,9	13,1	13,0
10,0	90,0	9,6	90,4	3,6	35,5	13,5	13,3
12,5	87,5	12,1	87,9	4,5	34,1	14,1	13,7
15,0	85,0	14,6	85,4	5,4	32,7	14,6	14,2
20,0	80,0	19,5	80,5	7,2	43,6	15,5	15,3

*Content of water molecules was calculated from the amount of H, % obtained from the CHN-analyzer.

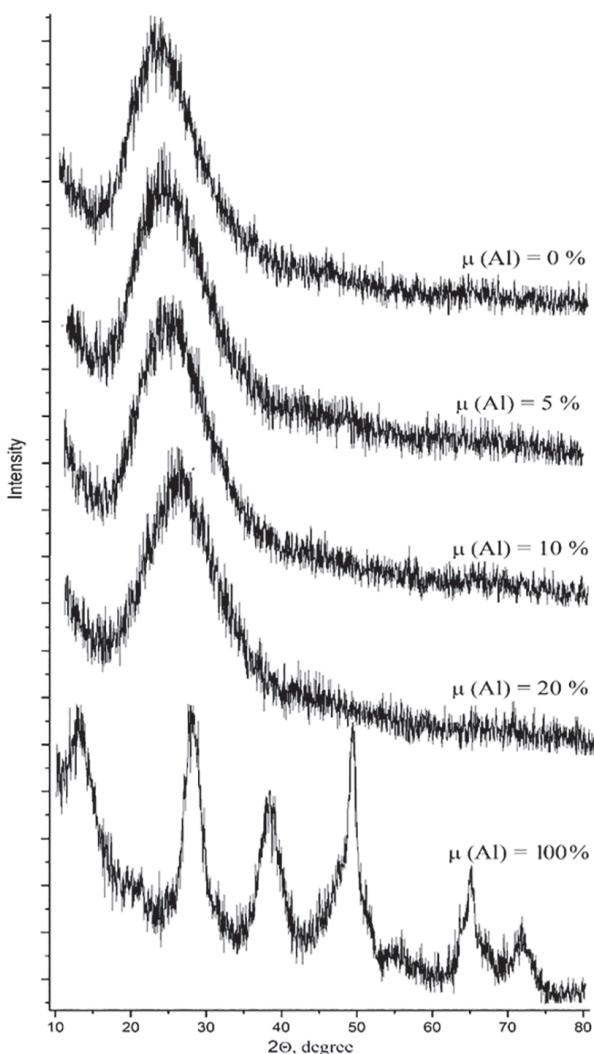


Fig.1. XRD patterns of xerogels synthesized from tetraethoxysilane and aluminum isopropoxide at various ratios

XRD patterns of the materials (Fig. 1) indicate that the samples are X-ray amorphous in the range $10^\circ \leq 2\theta \leq 90^\circ$. All diffraction patterns exhibit broadened signals at $22\text{--}25^\circ$, which are characteristic of amorphous silicon dioxide. It is known that halo-like reflections can be caused by both amorphous and nanocrystalline states of the samples [14]. The dif-

fraction spectrum of the nanocrystalline state is a superposition of broad reflections from all possible crystallographic planes. The half-width of such scattering crystallites depends on their size according to the Selyakov – Scherrer formula [15]. However, diffraction patterns of materials with different concentrations of aluminum are characterized by the same half-width of the band at $2\theta \approx 23^\circ$. Consequently, the diffraction patterns of the samples indicate their amorphousness. In accordance with the literature data [16, 17] for amorphous powders, the position of the first signal in the diffractogram corresponds to the distance between structural units (d) in accordance with Bragg's law ($2d\sin\theta = n\lambda$). Based on the θ values obtained, this distance is approximately 4.30 \AA , which is close to the value obtained for pure (undoped) silicon dioxide (4.20 \AA), and probably corresponds to the distance between SiO_4 tetrahedra.

For comparison, the figure also shows an XRD pattern of a sample obtained by hydrolysis of pure aluminum isopropoxide. The position of the reflections at $2\theta \approx 13, 28, 38, 49, 65, 71^\circ$ corresponds to the diffractogram of boehmite ($\gamma\text{-AlOOH}$) obtained by the sol-gel method earlier [18]. None of these reflections are observed in samples based on mixed matrices, which indicates the absence of the formation of a boehmite phase in mixed systems.

In the IR spectrum of silicon dioxide obtained by the method used for mixed xerogels the following bands are present (Fig. 2). Deformation vibrations of the O-Si-O and Si-O-Si bonds appear as signals at 468 and 799 cm^{-1} , respectively. Symmetric and asymmetric vibrations of Si-O-Si bonds are at 970 and 1088 cm^{-1} . In addition, the hydroxyl groups

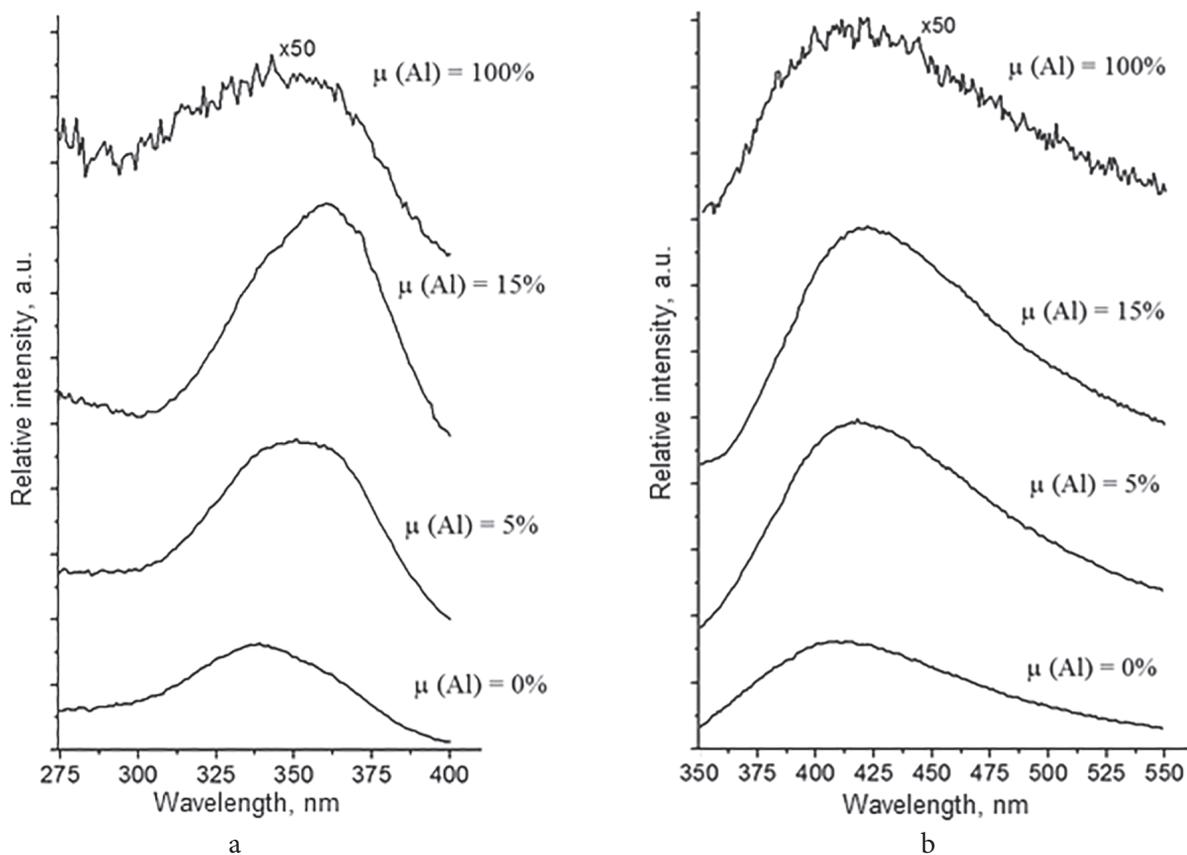


Fig. 4. Excitation (a) and luminescence (b) spectra of xerogels with different Si/Al ratios in comparison with pure alumina

Fig. 4 shows the excitation and luminescence spectra of the obtained xerogels, as well as pure aluminum hydroxide obtained by hydrolysis of aluminum isopropoxyl and pure silicon oxide obtained by hydrolysis of tetraethoxysilane.

In samples obtained by the sol-gel method from silicon alkoxides, an emission band in the region of 300–500 nm is often observed. Its nature was studied in most detail in [23–25], where the authors analyzed a large number of different processes, including “oxygen excess-related defects” or “oxygen deficiency-related defects”. However, in this study at least three different bands were observed in the range of 250–750

nm, while for amorphous silicon dioxide obtained by the sol-gel method, as a rule, one band is characteristic. The most intense fluorescence is observed in samples containing amino groups and amide fragments. The nature of this band has been studied by fluorescence, UV, visible, and IR spectroscopy, small-angle X-ray scattering spectroscopy and ^{13}C and ^{29}Si NMR in literature and may be caused by oxygen defects of the $\bullet\text{O-O-Si}(\equiv\text{O}_2\text{C})$ type arising in silica nanodomains [26–29]. Among other reasons causing it, the processes of charge transfer Si-O [30, 31], carbon, nitrogen and oxygen-containing impurities and accompanying defects [32, 33] are also indicated.

The position of the emission band in the luminescence spectra of xerogels depends on the wavelength of the exciting light. For example, in the case of pure (undoped) silica gel obtained with the same technique with increasing of the excitation wavelength, a bathochromic shift of the maxima is observed in both fluorescence and phosphorescence spectra (Fig. 5).

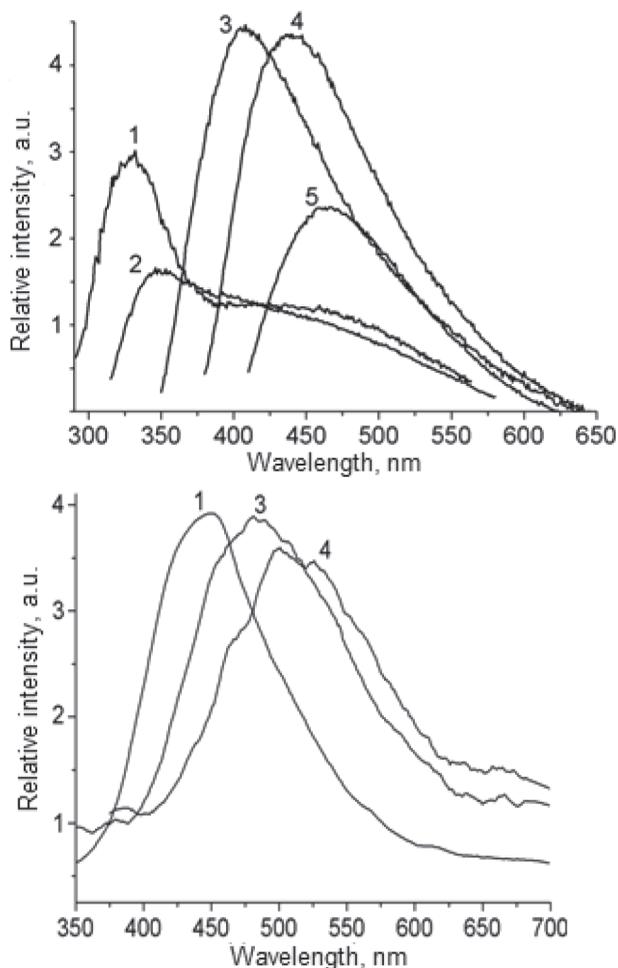


Fig. 5. Fluorescence (top) and phosphorescence (bottom) spectra of xerogel with $\mu(\text{Al}) = 15\%$ at different excitation wavelengths (280 nm (1), 300 nm (2), 330 nm (3), 370 nm (4), 395 nm (5))

This phenomenon is explained in [33] as follows. The resulting nanoclusters and domains have different sizes. High energy light quanta excite primarily domains with minimal sizes. Their subsequent relaxation through the electron-hole recombination mechanism leads to the emission of shorter-wavelength light. As the energy decreases, larger and larger domains are excited and emission is observed in the longer wavelength (visible) region. This can be confirmed by the red shift of the fluorescence maximum depending on the time of gel maturation, as well as the drying temperature (Fig. 6). Silica gel that has been dried at a higher temperature appears to emit in a longer wavelength range of the spectrum, since it is composed of larger nanoclusters.

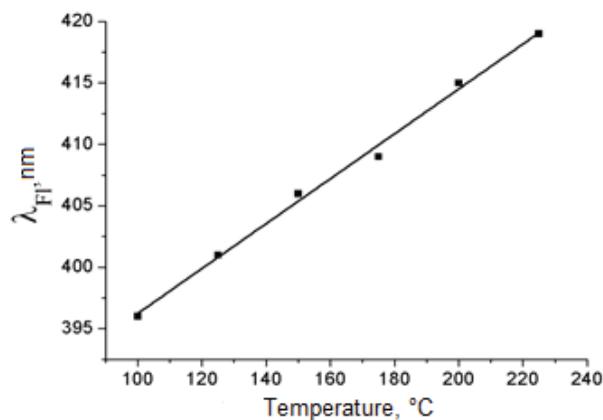


Fig. 6. Plot of the fluorescence maxima vs temperature of drying of xerogel with $\mu(\text{Al}) = 15\%$

The luminescence decay studies of obtained xerogels were also performed. It was found that luminescence decay of the pure silica gel is characterized by two-exponential function revealing two emitting states with lifetimes 5.7 and 17.7 ns. The addition of 5% aluminum led to a decrease of lifetimes - 3.8 ns and 11.0 ns. A further increase in the

aluminum concentration did not lead to a change in the decay kinetics up to 20% of alumina. It can be assumed that the appearance of aluminum atoms in the material matrix does not lead to the appearance of a new type of emitting centers, but affects the population of the already existing excited states. This fact may be caused by an increase of OH-oscillators due to higher water content as well as changes of the matrix polarizability, but it requires further studying.

Authors are grateful to the National Academy of Sciences of Ukraine for the financial support of this work.

CONCLUSIONS. In this work we investigated the synthetic conditions for obtaining $\text{SiO}_2\text{-Al}_2\text{O}_3$ materials with various Si : Al ratios via sol-gel method. Samples were characterized by means of elemental analysis, XRD, thermogravimetry and IR spectroscopy. It can be assumed that the introduced reagents are quantitatively transferred from the initial mixture to the composition of the formed samples. Fluorescence spectra of samples were analyzed. All samples shows fluorescence in the 300–500 nm region. The position of the emission band in the luminescence spectra depends on the wavelength of the exciting light, time of gel maturation and the drying temperature, which is the manifestation of the influence of the structure of units in xerogels on the luminescent properties. It can be concluded that $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixed matrix can serve as the inorganic host for luminescent lanthanide complexes which is the further development of this work.

$\text{SiO}_2\text{-Al}_2\text{O}_3$ КСЕРОГЕЛІ, ПРИГОТОВАНІ ЗОЛЬ-ГЕЛЬ МЕТОДОМ: СИНТЕЗ ТА ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ

С. С. Смола¹, Є. М. Фадєєв¹,
М. Ю. Русакова², Н. П. Єфрюшина¹,
Н. В. Русакова¹

¹Фізико-хімічний інститут ім. О. В. Богатського НАН України, Люстдорфська дорога, 86, Одеса 65080, Україна

²Одеський національний університет ім. І. І. Мечникова, Дворянська, 2, Одеса 65082, Україна

*e-mail: natavrusakova@gmail.com

Ксерогелі $\text{SiO}_2\text{-Al}_2\text{O}_3$ з різними співвідношеннями Si : Al були синтезовані золь-гель методом (використовували два види синтетичних процедур) та охарактеризували за допомогою елементного аналізу, рентгенофазового аналізу, термогравіметрії та ІЧ-спектроскопії. Під час синтезу втрат прекурсорів не виявлено, а введені компоненти кількісно переносяться від вихідної суміші до складу сформованих зразків. Положення смуги люмінесценції в області 300–500 нм залежить від довжини хвилі збуджуючого світла, часу дозрівання гелю та температури висихання, що є проявом впливу структурних одиниць у ксерогелях на люмінесцентні властивості.

Ключові слова: золь-гель метод, діоксид кремнію, оксид алюмінію, фотолюмінесценція.

**SiO₂-Al₂O₃ КСЕРОГЕЛИ, ПРИГОТОВЛЕННЫЕ
ЗОЛЬ-ГЕЛЬ МЕТОДОМ: СИНТЕЗ
И ЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА**

С. С. Смола¹, Е. Н. Фадеев¹,
М. Ю. Русякова², Н. П. Ефрюшина,
Н. В. Русякова¹

¹Физико-химический институт им.
А. В. Богатского НАН Украины, Люст-
дорфская дорога, 86, Одесса 65080, Украина

²Одесский национальный университет
им. И. И. Мечникова, Дворянская, 2, Одесса
65082, Украина

*e-mail: natavrusakova@gmail.com

Ксерогели SiO₂-Al₂O₃ с различным соотношением Si: Al были синтезированы золь-гель методом (использовались два вида синтетических процедур) и охарактеризованы с помощью элементного анализа, рентгенофазового анализа, термогравиметрии и ИК-спектроскопии. Во время синтеза потерь прекурсоров не обнаружено, а введенные компоненты количественно переносятся из исходной смеси в состав сформированных образцов. Положение полосы люминесценции в области 300–500 нм зависит от длины волны возбуждающего света, времени созревания геля и температуры высыхания, что является проявлением влияния структурных единиц ксерогеля на люминесцентные свойства.

Ключевые слова: золь-гель метод, диоксид кремния, оксид алюминия, фотолюминесценция.

REFERENCES

1. Brinker C.J. Sol-gel science: the physics and chemistry of sol-gel processing / Brinker C. J., Scherer G.W. – London: Academic Press, 1990. – 908 p.
2. Dhatarwal P., Sengwa R.J. Structural and dielectric characterization of (PVP/PEO)/Al₂O₃ nanocomposites for biodegradable nanodielectric applications. *Advanced Composites and Hybrid Materials*. 2020. <https://doi.org/10.1007/s42114-020-00168-y>.
3. Hybrid materials: synthesis, characterization, and applications / ed. By KICKELBICK G. – Wiley, 2007. – 516 p.
4. Binnemans K. Lanthanide-based luminescent hybrid materials. *Chemical Reviews*. 2009. **109**: 4283.
5. Yan B. Recent progress in photofunctional lanthanide hybrid materials. *RSC Advances*. 2012. **2**: 9304.
6. Yatluk Yu.G., Zhuravlev N.A., Koryakova O.V., Neudachina L.K., Skorik Yu.A. New hybrid chelating sorbents with grafted 3-aminopropionate groups based on mixed silicon, aluminum, titanium, or zirconium oxides. *Russian Chemical Bulletin*. 2005. **54**: 1836.
7. Pang X., Zhang H., Yu X., Wang T., Geng L., Wang Y., Li Y. Synthesis and characterization of novel luminescent europium(III) hybrid materials with a host based on titania-mesoporous silica or alumina-mesoporous silica. *RSC Advances*. 2015. **5**: 84790.
8. Guo L., Yan B. Photoluminescent rare earth inorganic-organic hybrid systems with different metallic alkoxide components through 2-pyrazinecarboxylate linkage.

- Journal of Photochemistry and Photobiology A: Chemistry*. 2011. **224**: 141.
9. Yan B. Novel photofunctional hybrid materials (alumina and titania) functionalized with both MOF and lanthanide complexes through coordination bonds. *RSC Advances*. 2014. **4**: 38761.
 10. Kysil D.V., Vasin A.V., Sevostianov S.V., Degoda V.Ya, Strelchuk V.V., Naseka V.M., Piryatinski Yu.P., Tertykh V.A., Nazarov A.N., Lysenko V.S. Formation and luminescent properties of $\text{Al}_2\text{O}_3\text{:SiOC}$ nanocomposites on the base of alumina nanoparticles modified by phenyltrimethoxysilane. *Nanoscale Research Letters*. 2017. **12**: 477.
 11. Romero R., Santoyo V. R., Moncada Sánchez C. D., Rosales M. M. Effect of aluminum precursor on physicochemical properties of Al_2O_3 by hydrolysis/precipitation method. *Nova Scientia*. 2018. **10**: 83.
 12. Nampi P., Moothetty P., Berry F.J., Mortimer M., Warriar K. Aluminosilicates with varying alumina-silica ratios: synthesis via a hybrid sol-gel route and structural characterisation. *Dalton Transactions*. 2010. **39**: 5101.
 13. Krasil'nikov V.N., Baklanova I.V., Zhukov V.P., Medvedeva N.I., Tyutyunnik A.P., Samigullina R.F., Gyrdasova O.I., Melkozerova M.A. The luminescence properties of $\text{g-Al}_2\text{O}_3\text{:C}$ produced by precursor method. *Journal of Alloys and Compounds*. 2017. **698**: 1102.
 14. Kudrenko E.A., Shmyt'ko I.M., Strukova G.K. Structure of precursors of complex oxides of rare-earth elements prepared by solvent thermolysis. *Physics of the Solid State*. 2008. **50**: 924.
 15. James R.W. The Optical Principles of the Diffraction of X-rays. The Crystalline state – Vol II. London: G. Bell and Sons Limited, 1962. – 664 p.
 16. Carlos L.D., Bermudez V.D., Ferreira R.A. Sol-gel derived urea cross-linked organically modified silicates. 2. Blue-light emission. *Chemistry of Materials*. 1999. **11**: 581.
 17. Physics of disorder materials.ed. by D. Adler, H. Fritzche, S. Ovshinsky. – New York: Plenum Press, 1985. – 850 p.
 18. Yu Z., Wang C., Gu X., Li C. Photoluminescent properties of boehmite whisker prepared by sol-gel process. *Journal of Luminescence*. 2004. **106**: 153.
 19. Okuno M., Zotov N., Schmäcker M., Schneider H. Structure of $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses: Combined X-ray diffraction, IR and Raman studies. *Journal of Non-Crystalline Solids*. 2005. **351**: 1032.
 20. Iler R.K. The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica. – Wiley, 1979. – 866 p.
 21. Lange K.R. The characterization of molecular water on silica surfaces. *Journal of Colloid Science*. 1965. **20**: 231.
 22. Armistead C.G., Hockey J.A. Reactions of chloromethyl silanes with hydrated Aerosil silicas. *Transactions of the Faraday Society*. 1967. **63**: 2549.
 23. Skuja L. Optically active oxygen-deficiency-related centers in amorphous silicon dioxide. *Journal of Non-Crystalline Solids*. 1998. **239**: 16.
 24. Trukhin A., Poumellec B. Photosensitivity of silica glass with germanium studied by photoinduced of thermally stimulated luminescence with vacuum ultraviolet radiation. *Journal of Non-Crystalline Solids*. 2003. **324**: 21.

25. Cannas M., Agnello S., Boscaino R. Ultraviolet emission lifetime in Si and Ge oxygen deficient centers in silica. *Journal of Non-Crystalline Solids*. 2003. **322**: 129.
26. Fitting H. How to make silica luminescent? *Journal of Luminescence*. 2009. **129**: 1488.
27. Carlos L.D., Ferreira R.A., Pereira R.N. White-light emission of amine-functionalized organic/inorganic hybrids: emitting centers and recombination mechanisms. *The Journal of Physical Chemistry B*. 2004. **108**: 14924.
28. Fu L., Sa Ferreira R.A., Silva N.J.O. Photoluminescence and quantum yields of urea and urethane cross-linked nanohybrids derived from carboxylic acid solvolysis. *Chemistry of Materials*. 2004. **16**: 1507.
29. Nobre S.S., Lima P.P., Mafra L. Energy transfer and emission quantum yields of organic-inorganic hybrids lacking metal activator centers. *The Journal of Physical Chemistry C*. 2007. **111**: 3275.
30. Yoldas B.E. Photoluminescence in chemically polymerized SiO_2 and $\text{Al}_2\text{O}_3\text{-SiO}_2$ systems. *Journal of Materials Research*. 1990. **5**: 1157.
31. Garcia J., Mondragon M., Tellez C. Blue emission in tetraethoxysilane and silica gels. *Materials Chemistry and Physics*. 1995. **41**: 15.
32. Green W.H., Le K.P., Grey J. White phosphors from a silicate-carboxylate sol-gel precursor that lack metal activator ions. *Science*. 1997. **276**: 1826.
33. Brankova T., Bekiari V., Lianos P. Photoluminescence from sol-gel organic/inorganic hybrid gels obtained through carboxylic acid solvolysis. *Chemistry of Materials*. 2003. **15**: 1855.

Стаття надійшла 10.09.2020