

This value is 10 nm for polymers doped with the dye №1. Polymer PEPK doped with the dye DCM photoluminescence intensity maximum is shifted to the right per 10–15 nm from the analogous maximum for PVE. For polymers doped with the dye №1 this value is 9–12 nm.

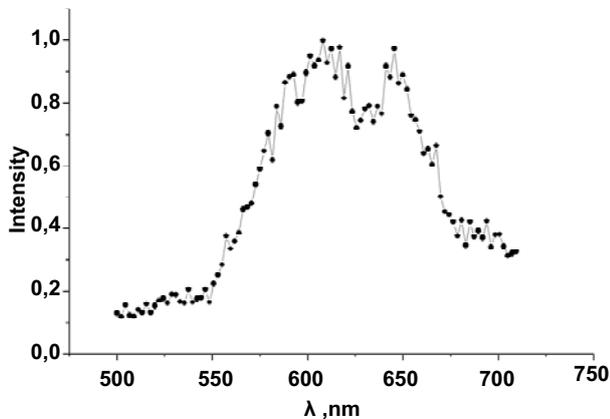


Fig. 8. Electroluminescence spectrum of the structure based on PPV at voltage  $V = 30V$

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#### ЛЮМИНЕСЦЕНТНІ ВЛАСТИВОСТІ ОРГАНІЧНИХ БАРВНИКІВ У ПОЛІМЕРАХ РЕРК І PVE

Виготовлено сандвіч-структури для дослідження електролюмінесценції шляхом нанесення органічного шару методом центрифугування на скляну підкладку з ITO та напылення алюмінієвих контактів і зразки для дослідження фотоліумінесценції. Досліджено залежність зміни положення максимумів спектрів фотоліумінесценції від вмісту барвника і типу матричного полімера. Знято вольт-амперні характеристики виготовлених сандвіч-структур та встановлено залежність інтегральної інтенсивності електролюмінесценції від напруги.

**Ключові слова:** органічний барвник, РЕРК, PVE, ITO, сандвіч-структура, OLED, фотоліумінесценція, електролюмінесценція, PPV.

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#### ЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА ОРГАНИЧЕСКИХ КРАСИТЕЛЕЙ В ПОЛИМЕРАХ РЕРК И PVE

Изготовлено сандвич-структуры для исследования электролюминесценции нанесением органического слоя методом центрифугирования на стеклянную подкладку с ITO и напылением алюминиевых контактов и образцы для исследования фотоліумінесценции. Исследовано зависимость изменения положения максимумов на спектрах фотоліумінесценции от количества красителя и типа матричного полимера. Снято вольт-амперные характеристики изготовленных сандвич-структур и установлено зависимость интегральной интенсивности электролюминесценции от напряжения.

**Ключевые слова:** органический краситель, РЕРК, PVE, ITO, сандвич-структура, OLED, фотоліумінесценція, електролюмінесценція, PPV.

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The instability of electroluminescence and electrophysical characteristics of the samples at voltages more than 10–15 V are found. Polymers, doped with organic dyes demonstrate characteristics, which are analogous to based on PPV structure's characteristics and can be used as a material for OLED's active layer.

#### REFERENCE:

1. Prosta realizatsiya metodu pidrahunku fotoniv dlia doslidzhennia spectriv poverhnevobarjernih nanogeterostruktur / S.V. Bunak, V.V. Ilchenko, O.M. Okoronko, A.G. Shkavro // Visnyk Kyivskogo universytetu, seria Fizyko-matematychni nauky, 2007. – № 4, P. 249–254.
2. Kelvin probe and ultraviolet photoemission measurements of indium tin oxide work function: a comparison / J.S. Kim, B. Lägél, E. Moons et al. // Synthetic Metals, 2000, Vol. 111–112, P. 311–314.
3. Structure and electronic properties of poly (3,4-ethylene-dioxythiophene) poly(styrene sulfonate) prepared under ultrasonic irremission / O. Yu. Posudievsky, N. V. Konoshchuk, A. G. Shkavro et al. // Synthetic Metals, 2014, Vol. 195, P. 335–339.
4. Issledovanie vliyania rassvoroiteley sopriazhennykh polimerov na harakteristiki planarnykh heterostruktur ITO/PEDOT:PSS/PF/AL I ITO/PEDOT:PSS/MEH-PPV/AL / V. M. Sorokin, Yu. V. Kolomzarov, M. A. Miniaylo et al. // Doklady BGUIR, 2011. – №3(57). – P. 81–86.

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#### PL AND FTIR SPECTROSCOPY OF POWDERED SILICA AEROGEL ar-SiO<sub>x</sub>

Optical and photoluminescent properties of powdered silica aerogel ar-SiO<sub>x</sub> have been investigated using FTIR spectroscopy and PL lifetime spectroscopy. Powdered silicagel was prepared from sodium silicate water solution using sol-gel technique. It was confirmed that the investigated material consists of two phases: stoichiometric SiO<sub>2</sub> and non-stoichiometric SiO<sub>x</sub>. FTIR analyses reveal the presence of numerical hydroxyle groups which determines oxidative properties of the material and makes it a promising matrix for the incorporation of nanoparticles. The intense PL emission was detected in blue-green region with stipulated peaks at 1.9, 2.0, 2.2 and 2.6 eV. It was shown that emission properties of powdered silica aerogel ar-SiO<sub>x</sub> caused by the presence of numerical oxygen defect centres: oxygen hole centers, peroxide radicals and oxygen-deficient centers as well as siloxane and silane groups. It was also obtained that under UV treating by pulsed laser irradiation the transformation the integrated PL intensity is decreased. The PL quenching is caused by transformation of the defect structure during photo oxidation process.

**Keywords:** powdered silica aerogel, defect states, FTIR transmission spectroscopy, PL lifetime spectroscopy.

**Introduction.** It is considered that porous oxide materials, possessing a large specific surface area, high porosity and fine grain structure, can be used as a comprehensive matrix for nanoparticles incorporation and molecular adsorption in order to create luminescent nanocomposites, photodetectors, catalysts, waveguides, lasers and gas sensors [1, 5, 12, 15]. The considered

nanoporous materials are simple and inexpensive in preparation, the gas sensor sensitivity can be significantly increased due to the enlarged overall active surface area.

The fact that typical aerogels have more than 90% porosity gives them unusual characteristics: they are characterized by extremely high surface area, high thermal resistivity, low dielectric constant and low refractive index.

Depending on the preparation technique the silica aerogel demonstrates a strong visible PL in the blue–green region [3]. Numerous studies have been devoted to the investigation of the origin of luminescence in other  $\text{SiO}_2$  based structures [2,17]. In fact, the structural and compositional features of the prepared silica aerogels, amorphous silica, silica xerogels and porous silica remain similar. In these materials, the ratio of surface atoms to bulk atoms is quite large, resulting in several potential light-emitting defect centres that are peculiar to the surface states. These surface related defect sites strongly affect the dynamics of the electronic transitions and will hence influence the related optical and PL properties.

In our earlier work [9] it was proved that silica aerogel has a high sensitivity with respect to liquid adsorbate and can be effectively used as transducer for chemical sensors. In this work optical and photoluminescence properties of powdered silica aerogel  $ar - \text{SiO}_x$  have been investigated. The effect of UV irradiation on evolution of PL spectra has been studied.

**Experiment.** Powdered silica aerogel ( $ar - \text{SiO}_x$ ) was prepared from sodium silicate water solution and an ethanol-based catalyst [11]. The drying process was carried out in an autoclave at supercritical parameters ( $T=240^\circ\text{C}$  and  $p=8 \cdot 10^6 \text{ Pa}$ ) in the presence of ethanol. These conditions are maintained for a short time with subsequent slow pressure reduction down to atmospheric pressure. As prepared material was then annealed at  $450^\circ\text{C}$  at oxygen atmosphere. The TEM image of porous  $ar - \text{SiO}_x$  is presented on Fig. 1. In our earlier work using X-ray diffraction analyses it was observed that porous aerogel  $ar - \text{SiO}_x$  is the mixture of amorphous and crystal phases that consists of cristobalite and quartz.

FTIR measurements were carried out using Fourier spectrometer "Perkin-Elmer Spectrum BX" in the range of  $400\text{--}4000 \text{ cm}^{-1}$  with  $4 \text{ cm}^{-1}$  resolution.

The samples used for PL measurements were prepared by pressing of silica aerogel into pellets with diameter of about 12 mm and typical thickness of  $0,2 \pm 0,3 \text{ mm}$  at a pressure of 13 MPa. The temporal domain PL spectra were measured at the room temperature using the analogous registration scheme [4]. The samples were excited with nitrogen laser pulses at 337 nm (3.68 eV), repetition rate 100 Hz, pulse duration  $\tau=8 \text{ ns}$  and average power 20 mW. The proper band of emission was selected by a monochromator (MS2004, SOLAR TII) and registered by a combination of photomultiplier (HAMAMATSU C6270) and analog-to-digital board (up to 1 GHz sample rate). The signal was processed and analyzed by PC.

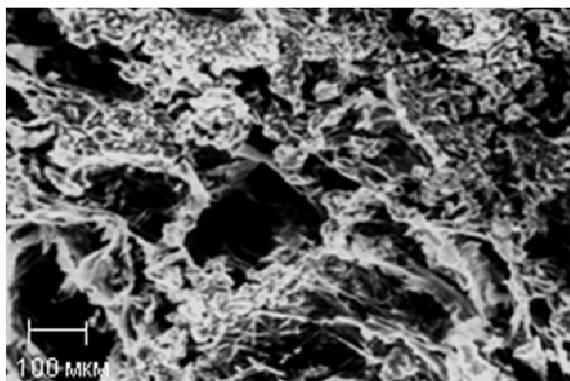


Fig. 1. TEM image of silica aerogel

**FTIR spectroscopy.** Fig. 2 shows FTIR transmittance spectrum of silica aerogel  $ar - \text{SiO}_x$ . There are absorption modes of  $\text{Si-O-Si}$  bonds with maxima at 1095, 780 and  $460 \text{ cm}^{-1}$  and a wide band in the  $3000\text{--}3700 \text{ cm}^{-1}$  region. The last one is due to the presence of adsorbed water and surface OH groups (OH stretching vibrations at  $3440 \text{ cm}^{-1}$ ) [6,14].

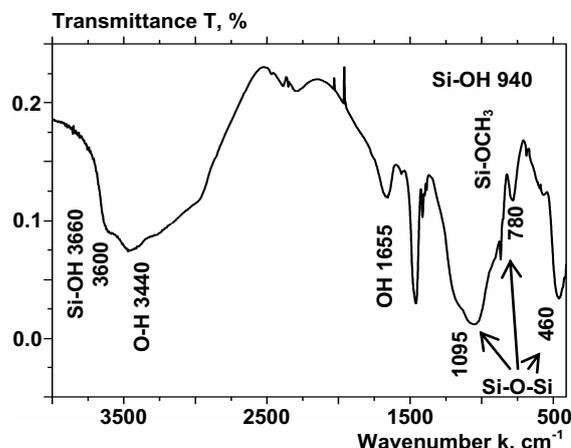


Fig. 2. FTIR transmittance spectrum of silica aerogel  $ar - \text{SiO}_x$  correlated by KBr spectrum. Characteristic absorbing modes are indicated

The nature of surface groups of silica aerogel is strongly dependent on the conditions used during its preparation. In the considered aerogel  $ar - \text{SiO}_x$  produced from water solution the surface is almost fully covered with hydroxyl groups.

Water molecules in interaction with silica surface groups effectively break  $\text{Si-O-Si}$  bonds forming a surface hydroxyl  $\text{Si-OH}$  groups, as a result FTIR spectrum reveals shoulders at  $3600$  and  $940 \text{ cm}^{-1}$  due to presence of bounded  $\text{Si-OH}$  groups.

A weaker  $\text{Si-OH}$  bending vibration band is revealed at  $1650 \text{ cm}^{-1}$ . The FTIR spectrum reveals also the presence of absorption modes of more complex structural groups such as  $\text{Si-OCH}_3$ .

In Fig. 3 the result of Gaussian peak deconvolution is presented for absorption peak of  $\text{Si-O-Si}$  stretching vibration LO and TO groups. The peak in the region of  $1300\text{--}850 \text{ cm}^{-1}$  has been revealed to have complex structure with maxima at 902, 1001, 1098 and  $1201 \text{ cm}^{-1}$ .

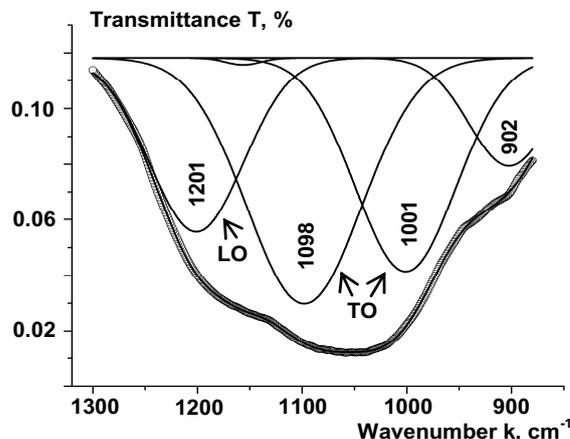


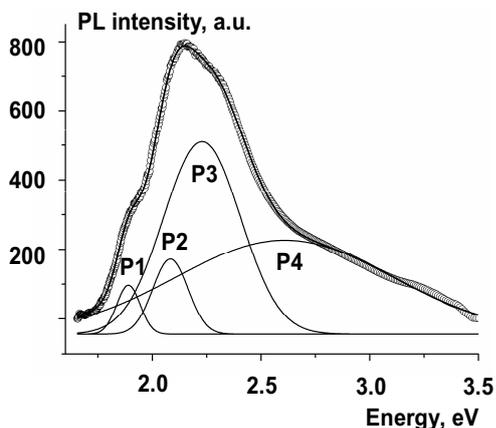
Fig. 3. The result of deconvolution into Gaussian profiles of stretching absorption  $\text{Si-O-Si}$  band of silica aerogel  $ar - \text{SiO}_x$

The presence of stretching TO modes at 1098 and 1201  $\text{cm}^{-1}$  having a large semiwidth (110 and 96  $\text{cm}^{-1}$  correspondingly) suggests that investigated material consists of stoichiometric and non-stoichiometric phases  $\text{SiO}_2 / \text{SiO}_x$ .

This conclusion is consistent with the data of X-ray diffraction analyses obtained in [10]. The wavenumber of TO absorption peak is calculated from empirical solution  $\nu(\text{SiO}_x) = 900 + 90x \text{ cm}^{-1}$  [6], so in our case  $x$  value varies from 1.1 to 2. Absorption peak at 1201  $\text{cm}^{-1}$  is also shifted from 1250  $\text{cm}^{-1}$  for stretching LO vibrations in stoichiometric  $\text{SiO}_x$  structures.

Taking into consideration the huge surface area and a number of surface hydroxyl groups, silica aerogel displays acidic properties and can be used as matrix for grafting of different molecules, e.g. for chemical sensors. In earlier work [17] it was proved that silica aerogel  $\text{ar-SiO}_x$  is characterized by significant sensor response under interaction with liquid adsorbates.

**PL spectroscopy.** The integrated PL spectrum of the freshly prepared  $\text{ar-SiO}_x$  sample is presented on Fig. 4. Gaussian peak decomposition of the PL spectrum reveals the presence of 4 basic peaks: Peak P1 at 1.89 eV with semiwidth (FWHM)  $\Delta E = 0.11$  eV; Peak P2 at 2.08 eV ( $\Delta E = 0.16$  eV); Peak P3 at 2.23 eV ( $\Delta E = 0.35$  eV) and Peak P4 at 2.61 eV ( $\Delta E = 0.99$  eV). The energy of all the maxima is smaller than the band gap of stoichiometric  $\text{SiO}_2$  structure which is 8.2 eV. However, in the case of nonstoichiometric structure  $\text{SiO}_x$  the band gap is smaller and can reach 1.1 eV for  $x=0$ . The FTIR transmittance spectra revealed the combination of stoichiometric and nonstoichiometric phases in  $\text{ar-SiO}_x$ , so it should be considered that the aerogel emission is associated with the presence of a  $\text{SiO}_x$  structure ( $1 < x < 2$ ) as well as with surface and bulk defect states in  $\text{SiO}_2$  phase.



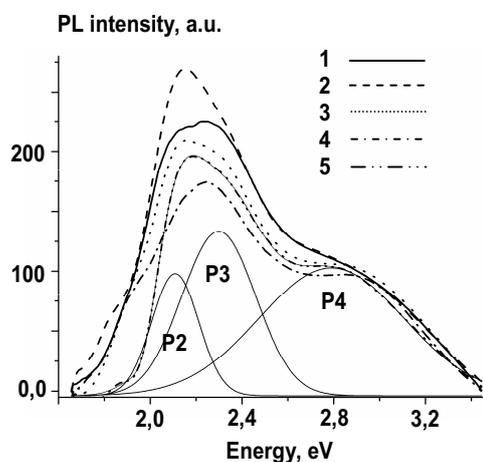
**Fig. 4. Integrated PL spectrum of freshly prepared  $\text{ar-SiO}_x$  sample.**  
Result of deconvolution into Gaussian profiles is shown

The structure of material and defect states are determined by preparation technology (temperature during the process of gel formation, concentration of reagents, pH level, etc.) [3,7,8]. Silica aerogels have several types of microstructural defects that can give contribution to the photoemission [3]. If PL excitation energy is 3.68 eV (nitrogen laser), the contribution to the photoemission of stoichiometric  $\text{SiO}_2$  phase can produce only defects determined by the interaction within individual  $\text{SiO}_x$  tetrahedra. These include defects with dangling bonds: 1)

non-bounded oxygen hole center (NBOHC), which is described as follows:  $\equiv \text{Si}-\text{O}\cdot$  where the dot means the unpaired electron; 2) peroxide radicals (POR)  $\equiv \text{Si}-\text{O}_2\cdot$  and 3) oxygen-deficient centers (ODC) which include oxygen vacancies and divacancies and two-coordinate silicon (ODC(II)) [16].

Oxygen hole centers are responsible for emission in low-energy region at around 1.8–1.9 eV. (Peak P1), while the maximum at 2.7 eV (P4) is associated with the presence of two coordinate silicon in  $\text{SiO}_x$  matrix. The emission peak at 2.08 eV arises due to the presence of siloxane ( $\equiv \text{Si}-\text{O}-\text{Si} \equiv$ ) and silane ( $\equiv \text{Si}-\text{O}-\text{H}$ ) groups. These groups are formed from hydroxyl  $\text{Si}-\text{OH}$  groups connected with hydrogen bonds during the dehydration process and due to the presence of silane ( $\text{SiH}$  and  $\text{SiH}_2$ ) in hydrogenated aerogels [3]. Peak P3 at 2.23 eV results from radiative recombination processes in nonstoichiometric structure  $\text{SiO}_x$  [7]. There is also the emission peak of peroxide radicals in this range.

**The influence of UV irradiation on luminescence properties of  $\text{ar-SiO}_x$ .** It was shown in our earlier work [10] that emission properties of porous composite materials based on silica aerogel essentially depend on storage conditions and external factors such as temperature, atmospheric humidity etc. Taking into consideration the fact that the PL emission properties of  $\text{ar-SiO}_x$  mostly caused by the presence of oxygen bonds and oxygen centers in dielectric matrix it's important to study the influence of UV irradiation on PL properties material under investigation. For this purpose we used pulse laser irradiation ( $\lambda = 337$  nm,  $p = 20$  mW) focused on the sample surface with beam diameter of 3–4 mm. Fig. 5 shows the evolution of the integrated PL spectra with increasing of irradiation time.



**Fig. 5 The evolution of PL spectra under pulsed UV irradiation ( $\lambda = 337$  nm) for  $\text{ar-SiO}_x$  sample:**  
1 – initial sample and after 2–4 min; 3–8 min; 4–12 min; 5–25 min irradiation. Result of deconvolution into Gaussian profiles for spectrum 5 is shown

Taking into consideration the obtained data, it can be concluded that the interaction between oxide matrix and UV irradiation caused the decreasing of PL integrated intensity as well as changes of the PL spectral composition. The most significant changes were observed for the low-energy peak at 1.87 eV (P1), namely, after UV irradiation during 16 min there is a complete quenching of emission peak. More detailed analyses have been made through the procedure of Gauss peak decomposition. Fig. 6 shows the evolution of peak positions during the UV irradiation.

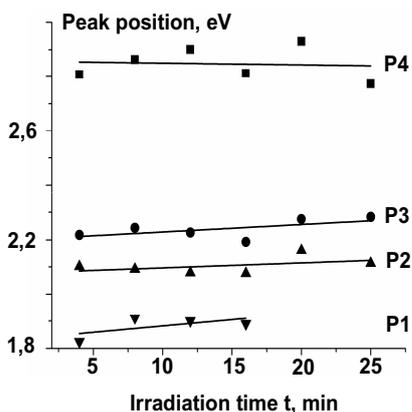


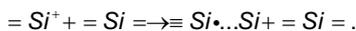
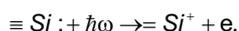
Fig. 6 The evolution of Gauss peak positions during UV irradiation for ar-SiO<sub>x</sub> sample

It could be clearly seen that under photo oxidation process the peak positions are almost unchanged except for a small shift of PL peaks at 2.1 eV (P2) and 2.2 eV (P3) towards the high energy region. At the same time there are essential changes in the peak intensity at 1.87 and 2.2 eV, namely after 16 min irradiation the low-energy peak disappears and the P3 peak area noticeably decreases. For two another peaks (P2 and P4) essential changes haven't been observed.

Thus for powdered silica aerogel the evolution of PL spectra during photo oxidation process under UV irradiation is mainly due to the transformation of emission peaks at 1.87 and 2.2 eV.

As mentioned above, the low-energy PL emission caused by the presence of oxygen-hole centers. During photo oxidation process the transformation of these vacancies to peroxide radicals occurs according to reaction:  $\equiv Si - O \cdot + O \rightarrow \equiv Si - O_2 \cdot$ .

It's also well known [13,16] that in amorphous silicon-oxide matrix under laser excitation there is a structural reorganization, namely transformation of the oxygen vacancies type ODC(II), such as divalent silicon  $Si_2^0$ , and the neutral oxygen vacancies (NOV) into defect type E' centers according to the scheme:



Since the E' centers can give a contribution to the photoemission under excitation energies of 5.8–6.3 eV, in our case, they are not active, which results in reducing of the peak intensity.

Thus, we can conclude that the decreasing of the integrated PL intensity of the powdered silica aerogel is caused by the transformation of the defect structure during photo oxidation process.

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## FTIR ТА ФЛ СПЕКТРОСКОПІЯ ПОРОШКОПОДІБНОГО АЕРОГЕЛЮ КРЕМНЕЗЕМУ ar-SiO<sub>x</sub>

Було досліджено оптичні та фотолюмінесцентні властивості порошкоподібного аерогелю кремнезему з використанням FTIR спектроскопії пропускання та фотолюмінесцентної спектроскопії. Порошкоподібний аерогель кремнезему було виготовлено на основі водного розчину силікату з використанням технології золь-гель синтезу. Підтверджено, що досліджуваній матеріал складається з двох фаз: стехіометричної SiO<sub>2</sub> та нестехіометричної SiO<sub>x</sub>. Аналіз FTIR спектрів пропускання виявив присутність значної кількості гідроксидних груп, що обумовлюють окиснювальні властивості матеріалу й визначають перспективність використання аерогелю кремнезему в якості ефективної матриці для інкорпорації наночастинок. Зарєєстровано інтенсивну ФЛ у синьо-зеленій області спектру з максимумами при 1.9, 2.0, 2.2 та 2.6 еВ. Було показано, що емісійні властивості порошкоподібного аерогелю кремнезему ar-SiO<sub>x</sub> обумовлені наявністю значної кількості кисневих дефектних центрів, таких як кисневі діркові центри, пероксидні радикали та киснево-дефіцитні центри, а також силосанових та силанових груп. Було також показано, що під впливом імпульсного лазерного УФ опромінення спостерігається зменшення інтегральної інтенсивності ФЛ. Гасіння ФЛ обумовлене трансформацією дефектної структури матеріалу в процесі фотоокиснення.

**Ключові слова:** порошкоподібний аерогель кремнезему, дефектні стани, FTIR спектроскопія пропускання, кінетика ФЛ.

**Conclusions.** In this work optical and photoluminescence properties of powdered silica aerogel ar-SiO<sub>x</sub> have been investigated using FTIR and PL spectroscopy. It was confirmed that investigated material consists of stoichiometric SiO<sub>2</sub> and non-stoichiometric SiO<sub>x</sub> phases. FTIR spectra revealed a presence of numerical hydroxyl groups such as bonded Si-OH and non-bonded -OH groups which determines oxidative properties of the material and makes it a promising matrix for incorporation of silicon nanoparticles.

Photoemission properties of investigated material are mainly due to the presence of oxygen defect states in non-stoichiometric SiO<sub>x</sub> phase as well as siloxane and silane groups. It was shown that UV irradiation causes the decreasing of integrated PL intensity of silica aerogel mainly due to the transformation of its defect structure.

### REFERENCE:

1. Porous silicon nanocrystals in a silica aerogel matrix / J. Amankosolpan, D. Wolverson, B. Goller et al. // *Nanoscale Research Letters.*, 2012. – Vol.7. – P. 397.
2. Ultraviolet excitation fine-tuning of luminescence bands of oxygen-deficient centers in silica / A. Anedda, C. Carbonaro, F. Clemente et al. // *J. App. Phys.*, 2002. – Vol. 92(6). – P. 3034.
3. Ayers M. Visibly photoluminescent silica aerogels / M. Ayers, A. Hunt // *J. Non-Cryst. Solids.*, 1997. – Vol. 217. – P. 229–235.
4. Influence of pH solution on photoluminescence of porous silicon / A. Benilov, I. Gavrilchenko, I. Benilova et al. // *Sens. Act. A.*, 2007. – Vol. 137. – P. 345–349.
5. Silicon nanoparticles in SiO<sub>2</sub> sol-gel film for nanocrystal memory device applications / A. Dima, F. Della Corte, C. Williams et al. // *Microelectronic Journal*, 2008. – Vol. 39. – P. 768–770.
6. Handbook of infrared spectroscopy of ultrathin films / Ed. by V. Tolstoy, I. Chernyshova, V. Skryshevsky. – N.J.: Wiley, 2003.
7. Hinić I. Influence of the synthesis conditions on the photoluminescence of silica gels / I. Hinić, G. Stanišić, Z. Popović // *J. of Serb. Chem. Soc.*, 2003. – Vol. 68(12). – P. 953–959.
8. Active Sites on Mesoporous and Amorphous Silica Materials and Their Photocatalytic Activity: An Investigation by FTIR, ESR, VUV-UV and Photoluminescence Spectroscopies / Y. Inaki, H. Yoshida, T. Yoshida et al. // *J.Phys.Chem. B.*, 2002. – Vol. 106(35). – P. 9098–9106.
9. Impedance spectroscopy of composites based on porous silicon and silica aerogel for sensor applications / A. Karlash, G. Kuznetsov, Yu. Milovanov et al. // *Functional Materials*, 2013. – Vol. 20, №1. – P. 110–117.
10. Evolution of visible photoluminescence of Si quantum dots embedded in silicon oxide matrix / A. Karlash, V. Skryshevsky, G. Kuznetsov et al. // *J. of Alloys and Compounds.*, 2013. – Vol. 577. – P. 283–287.
11. Photoluminescence properties of silica aerogel/porous silicon nanocomposites / A. Karlash, Yu. Zakharko, V. Skryshevsky et al. // *J.Phys.D: Appl. Phys.*, 2010. – Vol. 48. – P. 335–405.
12. Hierarchical nanostructured semiconductor porous materials for gas sensors / V. Moshnikov, I. Gracheva, V. Kuznezov et al. // *J. of Non-Cryst. Solids.*, 2010. – Vol.356(37–40). – P. 2020–2025.
13. Photoluminescence of oxygen-deficient-type defects in a-SiO<sub>2</sub> / N. Nishikawa, Y. Miyake, E. Watanabe et al. // *J. Non-Cryst.Sol.*, 1997. – Vol. 222. – P. 221–227.
14. Infrared studies of transition layers at SiO<sub>2</sub>/Si interface / H. Ono, T. Ikarashi, K. Ando et al. // *J. Appl. Phys.*, 1998. – Vol. 84. – P. 6064–6069.
15. Optical gain in silicon nanocrystals / L. Pavezi, L. Dal Negro, C. Mazzoleni et al. // *Nature*, 2000. – Vol. 408. – P. 440–444.
16. Skuja L. Optically active oxygen-deficiency-related centers in amorphous silicon dioxide / L. Skuja // *J. of Non-Cryst. Solids.*, 1998. – Vol. 239. – P. 16–48.
17. Yamada T. Photoluminescence property of transparent silica glass prepared from nanometer-sized silica particles / T. Yamada, T. Uchino // *J. of Optoelectr. and Adv. Mater.*, 2005. – Vol. 7(4). – P. 1935–1940.

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### FTIR И ФЛ СПЕКТРОСКОПИЯ ПОРОШКООБРАЗНОГО АЭРОГЕЛЯ КРЕМНЕЗЕМА $\alpha$ -SiO<sub>x</sub>

Проведено дослідження оптичних і фотолюмінесцентних властивостей порошкообразного аэрогеля кремнезема з використанням FTIR спектроскопії пропускання і фотолюмінесцентної спектроскопії. Порошкообразний аэрогель кремнезема ізогтовлюється на основі водного розчину силікату з використанням технології золь-гель синтезу. Підтверджено, що досліджуєму матеріал складає з двох фаз: стехіометричної SiO<sub>2</sub> і нестехіометричної SiO<sub>x</sub>. Аналіз FTIR спектрів пропускання виявив присутність значительного количества гідроксидних груп, котрі обумовлюють окислювальні властивості матеріалу і визначають перспективність його використання в якості матриці для інкорпорації наночастиць. Зареєстрована інтенсивна ФЛ в синьо-зеленої області спектра з максимумами при 1.9, 2.0, 2.2 і 2.6 эВ. Було показано, що емісійні властивості порошкообразного аэрогеля кремнезема  $\alpha$ -SiO<sub>x</sub> обумовлені наявністю значительного количества кислородних дефектних центрів, таких як кислородні дюрочні центри, пероксидні радикали і кислородно-дефіцитні центри, а також силіконові і силанові групи. Було також показано, що під впливом імпульсного лазерного УФ облучення спостерігається зменшення інтегральної інтенсивності ФЛ. Гашення ФЛ обумовлене трансформацією дефектної структури матеріалу в процесі фотоокислення.

**Ключевые слова:** порошкообразный аэрогель кремнезема, дефектные состояния, FTIR спектроскопия пропускания, кинетика ФЛ.

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### VISUALIZATION OF MAGNETO-ELECTRIC DISPLAYS IN FG/GGG EPITAXIAL STRUCTURES

Using the method of polarizing microscopy, under the combined effects of static and alternating electric fields and magnetic field, studied the reaction of the domain structure (DS) epitaxial ferrite garnet (FG) films, grown on single crystal substrates of gallium-gadolinium garnet (FG / GGG). In transmitted light visually detected a small effect of the profile changes ("smearing") of the individual local sites of the films domain wall (DW) because of a combination of three-channel external influence.

**Keywords:** magneto-electric effect, electric field, magnetic field, domain wall, domain structure, polarizing microscope.

**Introduction.** The change of magnetization under the influence of electric field or of electric polarization under the influence of magnetic field are called magnetoelectric (ME) effect. Study of the mechanism of interaction of electric and magnetic subsystems in magneto-electric materials has recently been the subject of many publications. This interest is driven by a need to establish a single fundamental theory of magneto-electric interactions in solids, and wide application possibilities of using magneto-electric materials in electronics.

The first explicit prediction of ME effect in a specific material was made by Dzyaloshinskii who showed that in Cr<sub>2</sub>O<sub>3</sub> these effects are allowed by the magnetic symmetry [2]. Experimentally, the electrically induced ME effect was first observed by Astrov [1] on a crystal of Cr<sub>2</sub>O<sub>3</sub> and later Rado and Folen [10]. The first observation of the ME effect in yttrium-iron-garnets (YIG) was reported by O'Dell [9] and later, the ME effect was studied in a number of papers [3+8, 12]. The external electric field that connected to the crystal of certain magnetic symmetry (eg, YIG), can cause in crystal the manifestations induced optical phenomena, linear or nonlinear in the electric field. One of such phenomenon is the effect of the changes of light polarization plane Faraday rotation in an optically transparent dielectric crystal induced by an electric field, which the authors named as an electromagneto-optical (EMO) effect [8]. Using a highly sensitive method of optical polarimetry, it is possible to measure the changes of light polarization plane rotation in an external electric field, as well as to carry out visual observations of the domain structure of the sample using a polarizing microscope.

Iron garnets are a large class of ferrimagnetic oxides with high Curie temperature ( $T_c > 500\text{K}$ ) and have been applied to magneto-optical devices and magnetic bubble memories [11, 13]. The active interest in the structural, magnetic, and magneto-optical properties of garnet films has been related to the fact that all these properties can be widely varied by changing the composition and orientation. Although the parent garnet crystal structure is characterized as the cubic centrosymmetric space group the studies of film structure and magnetic properties have revealed that films tend to have uniaxial or orthorhombic

symmetry. The origin of this symmetry lowering is due to growth anisotropy and mismatch between the lattice parameters of the films and substrates. The crystallographic orientation of the substrate is also of primary importance. Garnet crystals are well known to play an important role in technological devices.

Domain structure (DS) of ferrite garnets is periodically interspersed with small regions of antiparallel magnetization direction, which are separated by domain walls. In DW is changing the direction of the orientation of the spins in the same domain to the direction in the nearby. In ferrite garnets it is possible to visualize processes occurring in them due to the magneto-optical Faraday effect.

In this paper, we report the results of studies ME manifestations in epitaxial ferrite garnet films in a two-channel and three-channel external influence. In particular, visual observations were made for the DS of the film with the use of magneto-optical polarization microscopy with high optical permission based on the Faraday effect in two experimental versions: 1) under the joint action of the alternating electric field and constant magnetic field; 2) under the joint action of DC and AC electric field and a constant magnetic field. Investigated epitaxial films grown on (111) substrates of gallium-gadolinium garnets (GGG). The domain structure of the films studied under the polarizing microscope looks like high contrast, which indicates about significant deviation of domain magnetization vectors from the film plane.

**Experimental.** The test sample was placed between two optically transparent electrodes. The electrodes were deposited by spraying on the inner surfaces of the two thin glass plates. Separately or simultaneously to the sample plugged in the AC and DC voltage. External constant magnetic field was oriented along the plane of the film. The thickness of the film was about 10  $\mu\text{m}$ , the width of domains was about 14  $\mu\text{m}$  at  $H=0$ , and the domain-wall width was about 0.5  $\mu\text{m}$ . The test sample we previously several times been the iterative process of quasi-static magnetization in the magnetic field in both directions. The reproducibility of the overall picture domain labyrinth structure in this case was not observed. DW motion occurred intermittently due to the interaction with micro-