REVIEW

for obtaining the educational and scientific degree "Doctor" on the topic

'SPECTRAL AND PHYSICOCHEMICAL PROPERTIES OF AEROGEL COMPOSITE MATERIALS

in the professional field 4.2. Chemical Sciences (Physical Chemistry)

Dissertation: ***Dimitar Nikolaev Shandurkov***

Reviewer: ***Professor Tsonko Mitev Kolev***, PhD, Institute of Molecular Biology "Rumen Tsanev" - BAS

PhD student ***Dimitar Nikolaev Shandurkov***
declares that the presented dissertation on the topic: SPECTRAL AND PHYSICOCHEMICAL PROPERTIES OF AEROGEL COMPOSITE MATERIALS is his own development in his capacity as a PhD student at the Department of Physical Chemistry of the Faculty of Chemistry and Pharmacy. With scientific supervisor: Prof. Stoyan Ivanov Gutsov, PhD, Sofia University, Faculty of Chemistry
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Nationality: Bulgarian.
Dimitar Nikolaev Shandurkov has graduated from the Faculty of Chemistry
PIN: 9512012208. Born on: 01.12.1995 in Sofia. Gabrovo, region: Gabrovo country: Republic of Bulgaria, citizen of: Republic of Bulgaria enrolled in 2014 Graduated in 2018 Professional field: Chemical Sciences Specialty: CHEMISTRY

The dissertation is designed in a classical way.

1. Introduction. It is written on 4 pages and is very informative, tracing the development of materials science from ancient times to the present day. The dissertation convincingly shows that the development of civilization is related to the development of technology. He defines that composite materials can also be considered as frozen dispersions (solid collide solutions), and the dispersed phase can be micro or nano-sized. in the form of fibers or layers, in contrast to solid solutions, in which the subsidizing impurity is dispersed at the molecular level. The control of the chemical composition and microstructure of the dispersed phase becomes a lever for developing the functionality of the composites.

2. Goals and objectives of the dissertation.

The dissertation defines as the main goals of the dissertation the
a reproducible method for synthesis, hydrophobization and functionalization of silicate aerogel granules and study of the dependence of their textural and spectral properties on the degree of hydrophobization. The resulting systems are a series of porous amorphous SiO_2 with varying degrees of hydrophobicity and hybrid composites based on them with the complexes [Eu(phen)2](NO3)3 and [Tb(phen)2](NO3)3.

To achieve these goals, the following tasks have been set:

· Finding a reproducible physicochemical method for obtaining and hydrophobizing silicate aerogel granules.

Characterization of the silicate matrix by IR spectroscopy and low-temperature absorption and desorption isotherms.

· Development of a methodology for obtaining hybrid composites based on SiO2:[Eu(phen)2](NO3)3 and SiO2:[Tb(phen)2](NO3)3.

· Detailed study and description of the spectral properties of the obtained composites by spectra in diffuse reflection mode and emission and excitation spectra.

· Study of the influence of matrix hydrophobicity on the quantum yield of the resulting composite materials.

· Study of the microstructure of the obtained nanocomposites by diffraction and microscopic methods

For the purposes of the dissertation, hybrid composite materials based on silicate aerogels and the luminescent complexes bis-phenentroline europium trinitrate [Eu(phen)2](NO3)3 and bis-phenanthroline terbium trinitrate [Tb(phen)2](NO3)3 were obtained. The main goal is to obtain materials that combine the chemical resistance of silicates, the low thermal conductivity of aerogels and provide a matrix that protects the luminescent components from the environment - moisture, temperature and various mechanical impacts.

PhD student Shandurkov briefly describes the process: duringthe polycondensation reaction, a siloxane bridge (Si-O-Si) and a low molecular weight product – water or alcohol are formed. It is this process that leads to the formation of silicate oligomers. This increases the viscosity of the ash until the oligomers or individual particles bind to each other and form a gel. During the gelling process, there is a sharp jump in the viscosity of the system. catalyze from mineral acids, bases, ammonia, acetic acid or fluorides. The rate of reactions is strongly influenced by the pH of the medium, the molar ratio of water:precursor, temperature, solvent, as well as by the precursor itself.

A second important step, before drying the gel, is its aging. During the aging of the gel, the hydrolysis and polycondensation reactions are completed. The gel thickens, the average size of its pores increases, and its mechanical properties improve. The maturation of the gel can be facilitated by adding water and/or more monomeric units (TEOS) to react with non-hydrolyzed alkoxide groups or Si-OH groups.

The dissertation Standurkov is primarily interested in their physicochemical properties.

Aerogels are distinguished by their remarkable physicochemical properties.

The skeletal density of silicate gels is close to that of bulk silica (2.2 g/cm3), but due to high porosity, aerogels are the lowest density materials that are known (0.001-0.5 g/cm3) [8,23,24]. Usually, the volumetric part of the pores is more than 95% of the volume of the monolith, and most often aerogels belong to the mesoporous materials, that is, with a pore diameter between 5 and 100 nm. This class of materials is also distinguished by its extremely well-developed specific surface of 250-800 m2/g, but also those with a specific surface of more than 1000 m2/g have been obtained

Aerogels have very low thermal conductivity. At standard temperature and pressure (STP) it is about 0.02 W/mK and is lower than that of air – 0.025 W/mK.
This makes them one of the best insulation materials.

The main method for characterizing the products described in the dissertation is infrared spectroscopy, due to the relatively simple experimental techniques, easy sample preparation and clear interpretation of the spectra of many functional groups. It allows the analysis of known and unknown chemical compounds and mixtures, determination of the presence of different functional groups in materials, study of the structure and bonding in polymers, ceramics and glasses. determination of porosity and arrangement of structural elements of oxide gels, glasses and ceramics. The last region of the IR spectrum is the near IR region, which is located in the range of 4000-14000 cm-1. Various overtones and Raman oscillations of the molecules are observed there. In Bulgarian spectral literature, the word overtone is used, not overtone. The presence of Raman oscillations makes the analysis of spectra in the near IR region difficult. This method is particularly suitable for samples of known composition, which makes it easier to determine the origin of the stripes.
In IR spectroscopy, only transitions are observed that lead to a change in the dipole moment of the molecule in the process of normal oscillation. With a greater change in the dipole moment, as a result of the corresponding oscillation, a greater relative intensity of the corresponding transition in the IR spectrum of the molecule is expected. Transitions that lead to a change in the polarizability of the molecule are active in Raman spectroscopy. Analysis of the symmetry of the studied molecule and its placement in a certain group The symmetry can facilitate the analysis of its vibrational spectra. There are created reference books in which each group of symmetry is displayed, how many transitions are allowed, the number of degenerate states and which are IR and Raman active stripes. Notes: there is a discrepancy between citations 31, 32 and 33 of the Abstract and the Dissertation. There are no sources from 27 to 44 in the abstract.

3. Literature review.
It includes the following subsections: Aerogel materials.
Aerogels are a very broad and well-studied class of compounds for heat, sound and electrical insulation, but their high porosity allows the embedding of other components in their pores. The luminescent properties of europium and terbium ions have been studied and described in detail. Many hybrid complexes, ceramics and glasses are known, subsidized with these elements, which have luminescent properties. Most research has focused on pure luminescent components or their solutions. The compounds and properties of rare earth ions with 1,10-phenanthrolin, as well as a number of its derivatives, are described in detail. These complex compounds were chosen because of their ease of obtaining. Their low solubility in water and ethanol allows them to be obtained by minimal chemical preparation. Mixing solutions of rare earth ions and ligand 1,10-phenanthroline leads to the rapid precipitation of microcrystallites from the corresponding lanthanide complexes. This is exactly what Gutsov and co-authors used when they first obtained in situ and described this class of composite materials. All sub-points are well developed in the text of the dissertation, for which I give a very good assessment.
Methods of obtaining. Surface modification of aerogel materials.
Physicochemical properties. Aerogels are distinguished by their remarkable physicochemical properties.
The skeletal density of silicate gels is close to that of bulk silica (2.2 g/cm3), but due to the high porosity, aerogels are the lowest density materials known to us (0.001-0.5 g/cm3.

Aerogel composite materials containing lanthanide complexes. Mostlanthanide ions have luminescent properties. The intensity and color of the emitted radiation depend on the energy difference between the lowest excited level and the ground state. For the Eu^{3+} and Tb^{3+} ions, the most intense transitions are $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_5$, which give respectively the characteristic red and green color of the emissions of the two ions.

The transition energy for these ions is 12150 cm-1 and 14800 cm-1. Gd^{3+} has a very wide band gap (32000 cm-1) and emits in the ultraviolet region of the electromagnetic spectrum, so its complexes are not used among luminescent materials. Dy and Sm emit yellow and orange light, and systems based on Nd, Ho and Yb emit in the near-infrared region. I believe that the optical properties of rare earth elements are well represented in this subsection.

Functionalization of aerogel granules and powders.

Spectral methods for characterization of oxide sol-gel materials.

In this subsection, the PhD student describes the principles of the method and notes that peaks in IR spectroscopy do not appear as lines, but as bands of a certain width. This is due to anharmonic effects and inhomogeneous expansion. Theoretically, IR stripes are well described by Lorentz curves, often the profile changes due to peculiarities of the optical system of the spectrometer and the superimposition of more curves to a Gaussian or mixed profile. knowledge of vibration spectroscopy without having attended a specialized course.

Infrared spectroscopy of SiO_2. Model of the central powers.

Silica is made up of SiO_4^{2-} tetrahedra, which are arranged in different structures – chains and rings. There are also other non-condensed –OH groups and water molecules in the sample volume. The spectrum of amorphous silica A-SiO_2 has a number of stripes due to the different structures in the material and the remaining water. The peak at 1631 cm-1 is due to deformation oscillations of water molecules, and the wide strip at 3440 $^{cm-1}$ corresponds to the valence oscillation of the connection –O-H. The oscillations at 466, 620 and 800 $^{cm-1}$ are symmetrical and antisymmetric deformation oscillations of tetrahedra and hydroxyl groups. The model of central forces predicts the splitting of the strip into two – for transverse and longitudinal oscillation. Transverse oscillations are shifted to 1050 cm-1, and longitudinal oscillations about 1200 cm-1. compared to the spectrum of crystalline silica – quartz.

Physical foundations of the processes of absorption and emission of light.

Absorption and emission of Eu^{3+} and Tb^{3+} ions.

Luminescence spectroscopy. The first described luminescent coordination compounds (complexes), in which a metal ion is surrounded by one or more organic molecules with electron-donor properties, were described in the 1940s by Weissman 1942. salicylates, benzoates, and picrates, Weissman concludes that excitation efficiency is strongly influenced by the nature of the organic ligand, solvent, and temperature. Now, this process of energy transfer from the ligand to the activator ion is known as the "antenna effect." Crossby et al. prove that the triplet state of the ligand has a strong influence on the energy transfer process.

Quanta finished.

An excited electronic state can relax to a fundamental point through a number of processes, namely, radiative (fluorescence and phosphorescence) and non-radiative (vibrational and rotational transitions). Also, luminescence can be "extinguished" by various chemical substances or electronic energy can be transferred to a non-emitting form. The relative intensities of these processes are strongly influenced by the nature of the activator and its environment. Therefore, the measurement of quantum yield is a valuable approach in studying the photophysical properties of chromophores and the effect of their surroundings. Quantum yield (QY) is defined as the ratio of the number of Nem photons emitted to the number of absorbed such Nabs.

There are two experimental methods for measuring quantum mining, which can be most simply divided into the comparative method and the absolute method.

In the first method, the quantum yield of the test sample is obtained by comparing the emission and spectrum with that of a known standard. This method is very convenient for the study of weakly absorbing isotropic systems, for example, dilute solutions, but it has serious disadvantages. The selected luminescent standard shall have similar optical properties (absorption and emission) to the material under study. The comparative method turns out to be unsuitable for anisotropic samples, those in which the orientation and position of the sample would affect the measurement.

Quantum mining is found experimentally using an integrating sphere that can collect all the emitted light from the sample. This attachment also allows materials with a diameter of <<5 nm and does not have a large enough volume to form many layers.

Physical methods for characterization of porous materials.

Low-temperature isotherms of gas absorption-desorption.

Literature review – composite and luminescent materials. The last three subsections are given concisely and are quite informative

4. Experimental part.

Preparation and characterization of aerogel powders and granules.

For the production of silica gel granules, a two-step sol-gel technology described in the literature was used. The methodology is a modified version of the one developed by N. Danchova and co-authors, the main difference being that all steps are performed at room temperature. The following reagents were used: tetraethoxyorthosilane (TEOS) (Sigma, St.Louis, MO, USA), absolute ethanol (abs EtOH 99.6%) (Sigma), distilled water (dH2O), trimethylchlorosilane (TMCS) (Sigma); Acetone, N-hexane, hydrochloric acid and ammonia solution are supplied by local trading firms. All reagents used are of purity and have been used without additional purification.

IR spectroscopy – structure and hydrophobicity. Through IR spectroscopy, it is possible to determine what structural elements occur, as well as their arrangement (siloxane rings and chains, the valence angles between the building tetrahedra). From low-temperature isotherms, additional information can be extracted about the size of the pores, their shape, microstructure and morphology.

Preparation, photophysical properties and structure of luminescent composite materials based on SiO2:[Eu(phen)2](NO3)3 and SiO2:[Tb(phen)2](NO3)3. This subsection is the most important as it reflects the personal contributions of the PhD student.

Preparation of aerogel granules from SiO2 with varying degrees of hydrophobicity.

Hydrolysis is carried out for about 1 hour under constant stirring. The second step is the addition of 6 ml of the alkaline catalyst (cat G), which is a solution of ammonia in water and ethanol with a pH = 11. In a neutral and slightly alkaline environment, the polycondensation reaction is promoted, which leads to the creation of siloxane bridges and the production of oligomers, their cross-linking and bonding.

Fresh gels are coated with 20 mL abs EtOH and the solvent is exchanged in the pores and the gel matures for 24 hours. In this way, some of the unreacted molecules and formed salts in the pores of the gel are removed. The polycondensation reaction continues, and the gel becomes more measurable, which improves its mechanical properties.

IR spectroscopy – structure and hydrophobicity. Through IR spectroscopy, it is possible to determine what structural elements occur, as well as their arrangement (siloxane rings and chains, the valence angles between the building tetrahedra). From low-temperature isotherms, additional information can be extracted about the size of the pores, their shape, microstructure and morphology.

The author of the dissertation claims that the Röntgenostructural analysis shows that the samples obtained in this way are amorphous. A wide amorphous halo is observed and the well-defined diffraction peaks characteristic of crystalline phases are missing. The use of the word Röntgen is quite a gross mistake. The great German physicist Wilhelm Conrad Röntgen was the first physicist to receive the Nobel Prize.

5 Conclusions

1. A laboratory, subcritical procedure for obtaining hydrophobic silicate aerogols at room temperature has been successfully developed, whereby the powders have a specific surface area of 800–1000 m2 /g, an average pore diameter of 5–10 nm and a density of 0.2–0.3 g/cm3.
2. Analysis of the relative intensities of ATR-IR peaks of SiO2 in the range 900 – 1300 cm-1 is an effective method for tracking the surface hydrophobization of silicate powders with TMCS. The relative intensity of νthe as(SiOH) ATR-IR peak of SiO2 decreases during hydrophobization, which correlates with an increase in the relative intensity of νthe s(Si-CH) peaks. The process is accompanied by a rearrangement of the four- and six-membered siloxane rings in the aerogel matrix. 3. The textural properties of the obtained aerogel silicate micropowders depend on their degree of hydrophobicity. Analysis of the adsorption isotherms of nitrogen of these materials at 77 K leads to a calculated fractal coefficient of Ds = 2.80–2.50, as well as evidence of the existence of two types of nanopores: bottle-shaped and disk-shaped. 4. Obtained by a two-step procedure for the functioning of nanocomposites with a composition of SiO2:[Ln(phen)2](NO3)3; (Ln = Eu, Tb) are an amorphous, hydrophobic matrix in which nanocrystals of [Ln(phen)2](NO3)3 with an average size of 20-30 nm are embedded
5. The optical properties (emission spectra, excitation and quantum yield) of aerogel nanocomposites depend on the degree of hydrophobicity of the output aerogel matrix. The luminescence of the resulting materials is dominated by the presence of 1,10-phenanthroline→Ln3+ energy transfer and of O 2-→Ln3+ load transfer transitions. 6. The quantum yield of hybrid composites increases with their degree of hydrophobicity, reaching the values of the pure [Ln(phen)2](NO3)3 complex at 52 alpha = 1.5. The reason for this increase is in the chemical reaction of hydrophobization, leading to the removal of surface -OH groups. 7. The analysis of the luminescent spectra of hybrid nanocomposites proves the change in symmetry and chemical bonding at the molecular level of the complex [Ln(phen)2](NO3)3 when it is incorporated into the aerogel matrix. This result is correlated with röntgenostructural data, indicating the presence of a structural polymorphism of [Ln(phen)2](NO3)3. 8. The resulting hydrophobic aerogel composites have increased thermal stability compared to classical sol-gel materials. Functionalization with [Ln(phen)2](NO3)3, (Ln = Eu,Tb) nanocrystallites does not particularly alter the textural properties of hydrophobic aerogel granules. The physical properties of the obtained nanocomposites are favorable for the development of fluorescent sensors on this basis.

6. Contributions to the dissertation.

• For the first time, the hydrophobization of amorphous silica has been quantitatively described by analysis of ATP/IR spectra in the range of 900 - 1300 cm-1 and the formation of nanopores of different shapes during the hydrophobization of silica with TMCS has been proven. • A physicochemical methodology for functionalization of silicate aerogel garnules with complexes of [Ln(phen)2](NO3)3; Ln = Eu, Tb • Dependence of optical properties (emission spectra, excitation and quantum yield) of SiO2 aerogel nanocomposites was found: [Ln(phen)2](NO3)3; Ln = Eu, Tb of the degree of hydrophobicity of the output matrix. • Differences in the microstructure of the pure complexes [Ln(phen)2](NO3)3 and the composites SiO2: [Ln(phen)2](NO3)3 are shown, as well as the presence of structural polymorphism. • Increased thermal stability of the resulting hybrid aerogel composites compared to classical sol-gel composites has been demonstrated. • The aerogel nature of the resulting composites has been proven, a property suitable for the development of fluorescent sensors

7 Publications including dissertation results

1. D. Shandurkov, P. Ignatov, I. Spassova, S. Gutzov, Spectral and Texture Properties of Hydrophobic Aerogel Powders Obtained from Room Temperature Drying, Molecules 26 (2021) 1796 https://doi.org/10.3390/molecules26061796.
2. S. Gutzov, D. Shandurkov, N. Danchova, V. Petrov, T. Spassov, Hybrid composites based on aerogels: preparation, structure and tunable luminescence, J. Luminescence, 251 (2022) 119171. https://doi.org/10.1016/j.jlumin.2022.119171
3. D. Shandurkov, N. Danchova, S. Gutzov, Functional optical materials based on aerogels, Journal of Chemical Technology and Metallurgy, 2024 (in press), doi:10.59957/jctm.v59.i6.2024.XX
4. S. Gutzov, D. Shandurkov, N. Danchova, Aerogels – new materials with promising applications, e-Proceedings of the International scientific conference UNITECH 2021, 18.11 19.11.2021,Gabrovo,https://unitechselectedpapers.tugab.bg/images/papers/2021/UnitechSP_2021.pdf

8. Participation with reports at conferences, including results of the dissertation.

1. Dimitar Shandurkov, N. Danchova, V. Petrov, S. Gutsov, "Luminescent nanocomposite materials: preparation, structure and properties", XXI NATIONAL CONFERENCE ON CHEMISTRY FOR STUDENTS AND PHD STUDENTS, May 17-19, 2023, SOFIA. 2. Dimitar Shandurkov, Nina Danchova, Vesselin Petrov, Stoyan Gutzov, New Sol-Gel Composite Materials With Multicolour Emission: Physicochemical and Luminescent Properties, 8th International Sol-Gel Society Workshop SUSGEM 2023: SUSTAINABLE SOL-GEL ENERGY MATERIALS, 01-04 October 2023, Castelló (Spain). 3. Stoyan Gutzov, Dimitar Shandurkov, Nina Danchova, Functional optical materials, based on aerogels, 8. Balkan Conference on Glass Science and Technology, 25.09-27.09. 2023, Nessebar, Bulgaria. 4. Dimitar Shandurkov, Stoyan Gutsov, Veselin Petrov, New Composite Materials with Multicolor Emission: Physicochemical and Optical Properties, Belchin, 16-18 October, 202

9. Citations of publications included in the dessert.

Статията:Molecules (2021) (SCOPUS) се цитира от 1. Park, J., Jeong, M., Cho, Y.J., Kim, K.J., Tai, T.B., Shin, H., Lim, J.C., Chang, H.S., Investigation of tetrakis(ethylmethylamido)hafnium adsorption mechanism in initial growth of atomic layer deposited-HfO_2 thin films on H-/OH-terminated Si (100) surfaces (2023), Journal of Vacuum Science and Technology B, 41 (6), art. no. 062801 . 2. Yahya, E.B., Elarbash, S.S., Ben Moussa, S., Hajri, A.K., Abdullah Alzahrani, A.Y., Khalil, H.P.S.A., Microbial assisted date palm nanocellulose isolation and the fabrication of hydrophobic bioaerogel for oil absorption application, (2024) Industrial Crops and Products, 221, 3. Liu, B., Sun, L., Jin, F., Wan, Y., Han, X., Fu, T., Guan, Y., Xie, Z., Cheng, L., Tian, B., Feng, Z., A novel oleogel based on porous microgel from egg white, (2023) Food Hydrocolloids, 144, art. no. 109049. 4. Li, Z., Wang, Y., Wu, X., Liu, Q., Li, M., Shi, L., Cheng, X., Surface chemistry, skeleton structure and thermal safety of methylsilyl modified silica aerogels by heat treatment in an argon atmosphere , (2023) Journal of Non-Crystalline Solids, 611, art. no. 122335.
Статията в J. Luminescence (2022) SCOPUS се цитира от 5. Synthesis, crystal structure and luminescence properties of two novel Tb (III) complexes with 1, 10-phenanthroline derivatives as ligands, M Tsvetkov, D Elenkova, M Kolarski, R Lyapchev et al - Journal of Molecular Structure, 1314 (2024) 138768 6. Scanda K, Salas-Juárez CJ, Guzmán-Silva RE, Beltran HI, Garduño I, Guzmán-Mendoza J. Synthesis and photoluminescent spectroscopic analysis of lanthanum (III) coordinated with 1,10-Phenanthroline: A study of its thermally stable behavior. Spectrochim Acta A Mol Biomol Spectrosc. 2024; 325:125046. doi: 10.1016/j.saa.2024.125046.

I highly appreciate the citations of 2 of the articles included in the dissertation and I am convinced that the work is of high value.

10. References. Dimitar Shandurkov has cited 205 literary sources, which shows his knowledge of the scientific field in which he works.

A careful analysis of the experiments included in the dissertation shows that the work of PhD student Dimitar Shandurkov has led to his acquaintance with the most modern synthetic and instrumental methods for studying the physical and spectral relations of aerogel composite materials, which completed the educational part. The scientific part is completed with the presentation of the dissertation in the above-mentioned scientific publications in the impact factor specialized journals.

Critical Notes

When reading all the attached documents, I did not find any significant errors. Minor inaccuracies and spelling mistakes have been made. I have reflected the critical remarks in the relevant places in the review

Conclusion

Based on the in-depth analysis of the presented materials, I confidently state that PhD student Dimitar Nikolaev Shandurkov shows that he is a scientist with broad interests, despite his youth, including: synthesis, spectral and structural study of AEROGEL COMPOSITE MATERIALS and is a well-established specialist with good scientific experience. The significant scientific achievements of the candidate, the relevance and perspective of the results of her research give reason to confidently recommend to the Scientific Jury to fully accept the materials provided in the dissertation, to evaluate them positively, to select and propose

PhD student **Dimitar Nikolaev Shandurkov**

For obtaining the educational and scientific degree **"Doctor".** ***Field of higher education 4. Natural sciences, Mathematics, Informatics, Professional field, 4.2. Chemical Sciences – Physical Chemistry.***

Sofia 14.11.2024 Signature:.................

/prof. Tsonko Kolev/