

Condensed Matter and Interphases

Kondensirovannye Sredy i Mezhfaznye Granitsy

ISSN 1606-867X (Print)

https://journals.vsu.ru/kcmf/

Аннотации на английском языке

Original articles

Research article

https://doi.org/10.17308/kcmf.2023.25/11098

Biocatalysts based on papain associates with chitosan nanoparticles

S. S. Goncharova¹, Yu. A. Redko¹, M. S. Lavlinskaya^{1,2}, A. V. Sorokin^{1,2}, M. G. Holyavka^{1,2}, M. S. Kondratyev^{1,3}, V. G. Artyukhov¹ ¹Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

²Sevastopol State University,

33 Universitetskaya st., Sevastopol 299053, Russian Federation

³Institute of Cell Biophysics of Russian Academy of Sciences, 3 Institutskaya st., Pushchino 142290, Russian Federation Abstract

The research purpose was to develop and study biocatalysts based on papain associates with chitosan nanoparticles. We obtained medium and high molecular weight chitosan nanoparticles, both with and without ascorbic acid .

When the papainnanoparticles complexes with ascorbic acid were formed, the catalytic activity of the enzyme increased by 3 % for medium molecular weight chitosan and by 16 % for high molecular weight chitosan. After 168 hours of incubation in 0.05 M of Tris-HCl buffer (pH 7.5) at 37 °C, the free enzyme retained 15% of its catalytic activity, whereas its associates with chitosan nanoparticles exhibited ~ 30%. The papain complex with chitosan nanoparticles and ascorbic acid exhibited 40% of the enzyme catalytic activity.

We simulated the bonds and interactions within the chitosan-ascorbic acid-papain complex. The proposed biocatalysts have high prospects for effective use in cosmetology, biomedicine, and pharmacy.

Keywords: Nanoparticles, Papain, Chitosan, Association

Acknowledgements: The study was supported by Russian Science Foundation grant (project No. 21-74-20053, complexation of nanoparticles with enzymes).

For citation: Goncharova S. S., Redko Yu. A., Lavlinskaya M. S., Sorokin A. V., Holyavka M. G., Kondtatyev M. S., Artyukhov V. G. Biocatalysts based on papain associates with chitosan nanoparticles. *Condensed Matter and Interphases*. 2023;25(2): 173–181. https://doi.org/10.17308/kcmf.2023.25/11098

Research article

https://doi.org/10.17308/kcmf.2023.25/11099

Trap state and exciton luminescence of colloidal PbS quantum dots coated with thioglycolic acid molecules

I. G. Grevtseva, M. S. Smirnov, K. S. Chirkov, O. V. Ovchinnikov

Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

This work presents the results of studying the IR luminescence of colloid PbS quantum dots coated with molecules of thioglycolic acid. Luminescence of the sample was recorded using the InGaAs image sensor PDF 10C/M (ThorlabsInc., USA) and a diffraction monochromator with 600 mm⁻¹ grating. To study the temperature dependence of luminescence, the sample was cooled in a nitrogen cryostat down to 80 K. A redistribution of the luminescence intensity between two peaks (1100 and 1280 nm) was identified upon a decrease in temperature. It was shown that an exciton absorption peak was present in the excitation spectrum for the short-wave luminescence peak, and the Stokes shift was $\Delta E_{\text{stokes}} \sim 0.1$ eV. On the contrary, the exciton peak was absent in the luminescence excitation spectrum of the long-wave band, and its red boundary was shifted towards the short-wave region, that provided the Stokes shift of more than 0.3 eV.

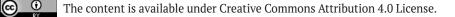
It was concluded that the short-wave luminescence band appeared as a result of the radiative annihilation of an exciton, while the longwave band appeared due to the recombination of charge carriers at trap states. Trap state luminescence was effectively excited upon direct absorption of the radiation by the luminescence centre. A three-level diagram was suggested that determined the IR luminescence of colloid PbS quantum dots coated with thioglycolic acid molecules.

Keywords: Lead sulphide quantum dots, Luminescence spectra, Excitation spectra

Funding: The study was supported by Russian Science Foundation grant No. 22-12-00232, https://rscf.ru/project/22-12-00232/

Acknowledgements: The results of transmission electron microscopy using a Libra 120 microscope were obtained with the help of the equipment of the Centre for Collective Use of Voronezh State University.

For citation: Grevtseva I. G., Smirnov M. S. Chirkov K. S., Ovchinnikov O. V. Trap state and exciton luminescence of colloidal PbS quantum dots coated with thioglycolic acid molecules. *Condensed Matter and Interphases*. 2023;25(2): 182–189. https://doi.org/10.17308/ kcmf.2023.25/11099



Research article

https://doi.org/10.17308/kcmf.2023.25/11100

Photoelectric response in sandwich structures based on condensed layers of Ag₂S quantum dots passivated with thioglycolic acid

V. S. Gurchenko¹, A. S. Mazinov¹, M. S. Smirnov^{2⊠}, I. G. Grevtseva², L. P. Nesterenko², O. V. Ovchinnikov²

¹V. I. Vernadsky Crimean Federal University,

4 prospekt Vernadskogo, Simferopol 295007, Republic of Crimea, Russian Federation

²Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

The study is aimed at developing a technique for forming a structure with a Schottky barrier in the form of a multilayer Al-Ag₂S-ITO sandwich structure, which includes a condensate of colloidal Ag_2S quantum dots passivated with thioglycolic acid molecules (Ag_2S /TGA QDs).

The spectral properties were studied using a USB2000+ spectrometer (Ocean Optics, USA) with a USB-DT light source (Ocean Optics, USA). Electrophysical and photoelectric properties of the structures were studied using a Keysight B1500A semiconductor device analyzer (Keysight tech, USA). The study of the temperature dependences of the properties in the temperature range from 300 to 360 K was carried out in a Shielded room (Faraday cage) placed in a muffle furnace. It was found that the conductivity of the Al-Ag₂S-ITO structure is mostly governed by the Schottky barrier at the Al-condensed Ag₂S QD film junction.

At the junction between the condensed Ag,S QDs film and Al, signs of the formation of a rectifying contact were found.

Under the action of the optical radiation with a wavelength of 650 nm and less, which corresponds to the most probable exciton transition in the UV-Vis absorption of Ag₂S/TGA QDs, an increase in the current was found for the negative branch of the J-V curve.

Keywords: Silver sulfide, Activation energy, Charge carrier mobility, Conduction mechanisms, Schottky barrier

Funding: The work was supported by a grant Russian Science Foundation № 22-12-00232

For citation: Gurchenko V. S., Mazinov A. S., Smirnov M. S., Grevtseva I. G., Nesterenko L. P., Ovchinnikov O. V. Photoelectric response in sandwich structures based on condensed Ag S quantum dots passivated with thioglycol acid. *Condensed Matter and Interphases*. 2023;25(2): 190–197. https://doi.org/10.17308/kcmf.2023.25/11100

Research article

https://doi.org/10.17308/kcmf.2023.25/11101

A comparison of the inhibitory activity of 3-alkyl- and 3-hydroxyalkyl-5-amino-1*H*-1,2,4-triazoles against copper corrosion in chloride-containing environments

D. V. Lyapun, A. A. Kruzhilin, D. S. Shevtsov, A. Yu. Potapov, Kh. S. Shikhaliev

Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

Copper is widely used as a material for technical solutions in microelectronics, as well as for the manufacture of various heat exchange equipment used in aggressive environments. Corrosion inhibitors are used for the reduction of the corrosive activity of the environment. This article presents the results of a study of the anticorrosion activity of a number of derivatives of the class 3-alkyl- and 3-hydroxyalkyl-5-amino-1*H*-1,2,4-triazole with respect to copper corrosion in chloride-containing environment. Over the course of the study, 3-alkyl- and 3-hydroxyalkyl-5-amino-1*H*-1,2,4-triazoles with different lengths of the alkyl substituent were synthesized. The structure of these compounds was confirmed using NMR spectroscopy and HPLC/MS analysis. Based on the results of electrochemical and direct corrosion tests, regularities were established for the inhibitory activity of the obtained compounds in acidic (1% HCl solution) and neutral (borate buffer solution, pH = 7.4) chloride-containing media.

In in a neutral media, the greatest protective effect was obtained for 3-propyl-5-amino-1H-1,2,4-triazole I, which has the shortest alkyl radical without modification by an OH group. As the concentration increased in the range from 0.01 to 10.0 mmol/L, the inhibitory activity increased. With an increase in the length of the alkyl radical and/or the introduction of an OH group, a decrease or absence of a protective effect was observed. At the same time, in an acidic medium, the introduction of a hydroxyl group into the alkyl substituent of 5-amino-1H-1,2,4-triazole increased anti-corrosion efficiency only with sufficient length of the carbon chain.

The highest protection degree was obtained for 17-(5-amino-1H-1,2,4-triazol-3-yl) heptadecan-7-ol **IV** at a concentration of 10.0 mmol/l and it reached a value of 97%.

Keywords: Metal corrosion, Copper, Corrosion inhibitors, Heterocyclic compounds, Aminotriazoles, Physico-chemical research methods *Funding:* The study was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of state order to higher education institutions in the sphere of scientific research for 2023-2025 (project No. FZGU-2022-0003).

Acknowledgements: Analytical and electrochemical studies were performed using the equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University.

For citation: Lyapun D. V., Kruzhilin A. A., Shevtsov D. S., Potapov A. Yu., Shikhaliev Kh. S. A comparison of the inhibitory activity of 3-alkyl- and 3-hydroxyalkyl-5-amino-1*H*-1,2,4-triazoles against copper corrosion in chloride-containing environments. *Condensed Matter and Interphases*. 2023;25(2): 198–206. https://doi.org/10.17308/kcmf.2023.25/11101

Research article

https://doi.org/10.17308/kcmf.2023.25/11102

Localization of the *E. coli* Dps protein molecules in a silicon wires matrix according to scanning electron microscopy and X-ray photoelectron spectroscopy

E. V. Parinova¹, S. S. Antipov^{1,2}, V. Sivakov³, E. A. Belikov¹, O. A. Chuvenkova¹, I. S. Kakuliia¹, S. Yu. Trebunskikh¹,

M. S. Skorobogatov¹, R. G. Chumakov⁴, A. M. Lebedev⁴, V. G. Artyukhov¹, S. Yu. Turishchev¹

¹Voronezh State University,

1 Universitetskaya pl., Voronezh, 394018, Russian Federation

²Institute of Cell Biophysics of the Russian Academy of Sciences,

3 Institutskaya st., Pushchino, 142290, Russian Federation

³Leibniz Institute of Photonic Technology, Department Functional Interfaces,

9 Albert Einstein st., Jena, 07745, Germany

⁴National Research Center "Kurchatov Institute",

1 Akademika Kurchatova pl., Moscow, 123182, Russian Federation

Abstract

The work is related to the study of the morphological features of silicon wires arrays combined with a nanomaterial of natural origin, a bacterial ferritin-like protein Dps, and their relationship with the composition of the surface and interior.

A silicon wires array was formed by metal-assisted wet chemical etching. To obtain recombinant protein, *Escherichia coli* BL21*(DE3) cells were used as producers, and purification was carried out by the chromatography method. The combination of silicon wires with protein molecules was carried out by layering under laboratory conditions, followed by drying. The resulting hybrid material was studied by scanning electron microscopy and X-ray photoelectron spectroscopy.

The initial silicon wires array had sharp boundaries on the surface. The diameter of the silicon wires was about 100 nm, while the distances between the wires can vary widely, reaching several hundred nanometres or be less than 100 nanometres, depending on the formation conditions, in the absence of noticeable transition layers. The pores formed in this way are available for filling with protein during deposition. The effectiveness of using the scanning electron microscopy method to study the morphology of the hybrid material "silicon wires – bacterial protein Dps" as well as X-ray photoelectron spectroscopy method together with ion etching for the investigation of the composition and physico-chemical of the hybrid material was demonstrated. Complementary results have shown that the molecular culture, which is a solution of oligomers of the recombinant Dps protein of *E.coli* bacterial cells, can penetrate deep into the pores of the silicon wires array with an extremely developed surface. The possibility of the control of the filling of silicon wires arrays by varying the pore morphology and other modes of formation of structures and their surface has been demonstrated.

The obtained data can be used to study the possibilities of the functionalization of the developed surface of silicon wires by their driven coating with controlled delivery of biohybrid material.

Keywords: Nanostructures, Biomolecules, Hybrid materials, Developed surface, Recombinant ferritin-like protein Dps, Silicon wires, Scanning Electron Microscopy, X-ray Photoelectron Spectroscopy

Funding: The study was supported by Russian Science Foundation (Project 19-72-20180). The work on silicon wire array formation and the methodology of work with protein molecules from E.coli cell material was supported under scholarship of the President of Russian Federation SP-189.2021.1 for young scientists.

For citation: Parinova E. V., Antipov S. S., Sivakov V., Belikov E. A., Chuvenkova O. A., Kakuliia I. S., Trebunskikh S. Yu., Skorobogatov M. S., Chumakov R. G., Lebedev A. M., Artyukhov V. G., Turishchev S. Yu. Localization of the *E.coli* Dps protein molecules in a silicon wires matrix according to scanning electron microscopy and X-ray photoelectron spectroscopy. *Condensed Matter and Interphases*. 2023;25(2): 207–214. https://doi.org/10.17308/kcmf.2023.25/11102

Research article

https://doi.org/10.17308/kcmf.2023.25/11103

Photosensitising reactive oxygen species with titanium dioxide nanoparticles decorated with PbS quantum dots A. S. Perepelitsa, S. V. Aslanov, O. V. Ovchinnikov, M. S. Smirnov, I. G. Grevtseva, A. N. Latyshev, T. S. Kondratenko

Voronezh State University,

1 Universitetskaya pl., Voronezh, 394018, Russian Federation

Abstract

The development of new efficient photocatalysts based on nanostructured materials with a wide range of photosensitivity in visible and near-infra-red regions and high efficiency of reactive oxygen species generation is an important task. The purpose of this project was to establish the possibility of photosensitising the process of generating reactive oxygen species (ROSs) with TiO₂ nanoparticles (NPs) decorated with colloidal PbS quantum dots (QDs) passivated with 3-mercaptopropionic acid (3MPA) as well as the possibility of increasing the spectral sensitivity of synthesised nanoheterosystems into the red region.

The paper analyses the photocatalytic properties of TiO_2 NPs with an anatase structure and average size of 12 nm decorated with colloidal PbS QDs with an average size of 2.7 nm passivated with 3MPA. It also provides structural and spectral substantiation of the formation of TiO_2 NPs – PbS/3MPA QDs nanoheterostructures. Absorption and luminescence techniques were used to establish the efficiency of generating various ROSs by TiO_2 NPs – PbS/3MPA nanoheterostructures and their individual components under excitation in the UV and visible radiation. It was shown that TiO_2 NPs decoration with PbS QDs extends the spectral range of sensitivity to the generation of reactive oxygen species in the UV to 1_7100 nm. The study revealed an increased efficiency of hydrogen peroxide generation by nanoheterostructures as compared to individual PbS QDs and TiO_2 nanoparticles.

Keywords: Nanoparticles, Titanium dioxide, Quantum dots, Lead sulphide, Photosensitisation, Reactive oxygen species, Photocatalysis *Funding*: The study was conducted within the framework of the state order to higher education institutions (FZGU-2023-0007) and the Ministry of Science and Higher Education of the Russian Federation under Agreement (N 075-15-2021-1351).

Acknowledgements: The studies of structural properties conducted by the methods of transmission electron microscopy and X-ray diffractometry were carried out using the equipment of the VSU Centre for Collective Use of Scientific Equipment.

For citation: Perepelitsa A. S., Aslanov S. V., Ovchinnikov O. V., Smirnov M. S., Grevtseva I. G., Latyshev A. N., Kondratenko T. S. Photosensitising reactive oxygen species with titanium dioxide nanoparticles decorated with PbS quantum dots. *Condensed Matter and Interphases*. 2023;25(0): 215–224. https://doi.org/10.17308/kcmf.2023.25/11103

Research article https://doi.org/10.17308/kcmf.2023.25/11104 The effect of the synthesis conditions on the crystal structure of palladium(II) oxide nanofilms A. M. Samoylov¹, S.S. Kopytin¹, S.A. Ivkov¹, E. A. Ratkov¹, E. A. Tutov² ¹Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

²Voronezh State Technical University, 84 20 letiya Oktyabrya st., Voronezh, 394006, Russian Federation

Abstract

Nanocrystalline films of palladium(II) oxide obtained by oxidation of the initial metallic Pd layers with a thickness of 35 nm on Si (100) substrates in atmospheric air were studied using XRD analysis, TEM, and RHEED.

PdO/SiO_/Si (100) heterostructures were synthesised in two stages. First, we obtained finely dispersed layers of metallic Pd on SiO_/Si (100) substrates with an ~ 300 nm SiO₂ buffer layer using thermal sublimation in a high vacuum. The Pd layers were then oxidised in the temperature range $T_{\rm ev}$ = 620 – 1100 K in atmospheric air (with the partial pressure of oxygen of about 21 kPa). The study determined that the deformation of the tetragonal crystal structure of homogeneous nanocrystalline PdO films is explained by an increase in the values of lattice parameters with the oxidation temperature. The deformation reaches its maximum values at $T_{ox} \sim 970$ K. Comparison of the obtained results with the earlier data regarding PdO/SiO₂/Si (100) heterostructures synthesised in a dry oxygen atmosphere (with the partial pressure of oxygen of about 101.3 kPa) demonstrated that PdO films synthesized in an oxygen atmosphere are characterized by a higher degree of deformation of the crystal structure.

The effect of the oxidation temperature and O, partial pressure on the increase in the tetragonal lattice parameters of the PdO films can be explained by the formation of interstitial oxygen atoms in the octahedral void in the centre of the palladium(II) oxide unit cell. Keywords: Palladium, Palladium(II) oxide, Heterostructures, Crystal structure, Gas sensors

Funding: The study was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of state order to higher education institutions in the sphere of scientific research for 2023-2025 (project No. FZGU-2023-0006).

Acknowledgements: Powder diffraction, transmission electron microscopy, and reflection high-energy electron diffraction studies were conducted using the equipment of the Centre for Collective Use of Scientific Equipment of VSU.

For citation: Samoylov A. M., Kopytin S. S., Ivkov S. A., Ratkov E. A., Tutov E. A. The effect of the synthesis conditions on the crystal structure of palladium(II) oxide nanofilms. Condensed Matter and Interphases. 2023;25(2): 225-236. https://doi.org/10.17308/ kcmf.2023.25/11104

Research article

https://doi.org/10.17308/kcmf.2023.25/11110

Phase relations in the Si-Sn-As system

T. P. Sushkova, G. V. Semenova, E. Yu. Proskurina

¹Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

²Voronezh State Technical University,

84 20 letiya Oktyabrya st., Voronezh, 394006, Russian Federation

Abstract

The goal of this work was to study phase relations in the ternary Si-Sn-As system: to establish cross sections, to construct a scheme of phase equilibria, and to identify the temperature of non-variant transformations.

Ternary alloys were obtained through direct synthesis from simple substances and subjected to long-term solid-phase annealing. Alloys of four polythermal sections of the Si-Sn-As system were examined using X-ray phase and differential thermal analysis. The results of X-ray powder diffraction allowed establishing that the phase subsolidus demarcations was performed by the SnAs-SiAs, SnAs-SiAs, Sn₄As_z-SiAs, and Sn₄As_z-Si sections.

As a result of the experiment, taking into account the theoretical analysis, we suggested a scheme of phase equilibria in the system that involved the implementation of eutectic and four peritectic invariant equilibria, and we used differential thermal analysis to determine the temperature of these four-phase transformations.

It was found that extended solid solutions were not formed in the system, and only a substitutional solid solution at least 3 mol % wide was formed based along the SnAs-SiAs, section based on tin monoarsenide.

Keywords: Phase diagram, Polythermal section, Si-Sn-As ternary system

Acknowledgements: X-ray powder diffraction studies were performed using the equipment of the VSU Centre for Collective Use of Scientific Equipment.

For citation: Sushkova T. P., Semenova G. V., Proskurina E. Yu. Phase relations in the Si-Sn-As system. Condensed Matter and Interphases. 2023;25(2): 237-248. https://doi.org/10.17308/kcmf.2023.25/11110

Research article

https://doi.org/10.17308/kcmf.2023.25/11105

Influence of UV radiation on the catalytic activity of nanosized cobalt ferrite in the oxidative degradation reaction of dinitrophenol

E. V. Tomina^{1,2}, Vo Quang Mai³, N. A. Kurkin¹, A. V. Doroshenko¹, Nguyen Anh Tien⁴, A. A. Sinelnikov¹

¹Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

²Morozov Voronezh State University of Forestry and Technologies,

8 Timiryazeva ul., Voronezh 394087, Russian Federation

³Sai Gon University,

273 An Duong Vuong Street, Ward 3, District 5, Ho Chi Minh City, Vietnam

⁴Ho Chi Minh City University of Education,

280 An Duong Vuong Street, Ward 4, District 5, Ho Chi Minh City, Vietnam

Abstract

Due to their multi-functionality, spinel ferrites, both doped and undoped, are promising materials for a wide range of practical applications, including catalysis, sustainable production of hydrogen and CO_2 deposition, electronic and magnet devices, as well as antibacterial agents. Recently, nanosized ferrites have been actively tested as catalysts in Fenton-like processes of deep oxidative degradation of organic substances in order to purify waste waters of different dyes, phenol and its derivatives, and antibiotics. The goal of this work was to establish the catalytic activity of $CoFe_2O_4$ nanopowder synthesised using citrate combustion in the reaction of oxidative degradation of 2,4-dinitrophenol upon the activation of the process with UV radiation.

Using citrate combustion, we synthesised the impurity-free nanopowder of $CoFe_2O_4$ cobalt ferrite with the average size of particles of about 70 nm and a pronounced agglomeration of particles. The cobalt spinel was tested as a catalyst of Fenton-like reaction of oxidative degradation of 2,4- dinitrophenol with UV radiation of λ = 270 nm. This process was differentiated with the sorption of dinitrophenol on a nanosized catalyst.

The degree of degradation of 2,4-dinitrophenol in a Fenton-like reaction without the $CoFe_2O_4$ catalyst was 14 %, while in the presence of a nanosized catalyst it increased up to 80 %. The effective oxidative degradation of the pollutant was performed in a less acidic environment as compared to a classic Fenton process with a rather large initial concentration of dinitrophenol. This allowed considering the nanosized $CoFe_2O_4$ as a promising catalyst of Fenton-like of waste waters purification through deep oxidative degradation of toxins.

Keywords: Catalysis, Nanosized ferrites, Wastewater treatment, Ultraviolet radiation

Acknowledgements: The study was supported by Russian Science Foundation grant No. 23-23-00122, https://rscf.ru/project/23-23-00122/ The research results were partially obtained using the equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University. URL: http://ckp.vsu.ru.

For citation: Tomina E. V., Vo Quang Mai, Kurkin N. A., Doroshenko A. V., Nguyen Anh Tien, Sinelnikov A. A. Influence of UV radiation on the catalytic activity of nanosized cobalt ferrite in the oxidative degradation reaction of dinitrophenol. *Condensed Matter and Interphases*. 2023;25(2): 249–256. https://doi.org/10.17308/kcmf.2023.25/11105

Research article

https://doi.org/10.17308/kcmf.2023.25/11106

Phase diagrams of zirconium dioxide systems with yttrium and scandium oxides

P. P. Fedorov, E. V. Chernova

Prokhorov General Physics Institute of the Russian Academy of Sciences,

38 Vavilova st., Moscow 119991, Russian Federation

Abstract

The literature data on the study of phase equilibria in systems zirconia with yttria and scandia are analysed. Possible schemes of lowtemperature phase equilibria in $ZrO_2-Y_2O_3$ and $ZrO_2-Sc_2O_3$ systems are presented taking into account the third law of thermodynamics. The coordinates of non-variant transformations in these systems are tabulated. A sign of non-equilibrium states is the observation of non-diffusion processes of ordering of solid solutions. The modified cryoscopy method is used to calculate the distribution coefficients of scandia and yttria during the crystallization of the ZrO_3 melt.

The possibilities for the existence of a set of ordered phases in the ZrO_2 - Y_2O_3 system and diffuse phase transition in the cubic modification of zirconia are discussed.

Keywords: Zirconia, Yttria, Scandia, Solid solutions, Ordering, Phase diagrams, Distribution coefficients

Funding: The study was supported by a grant from the Russian Science Foundation No.22-13-00167 https://rscf.ru/project/22-13-00167 *For citation*: P. P. Fedorov, E. V. Chernova. Phase diagrams of zirconium dioxide systems with yttrium and scandium oxides. *Condensed Matter and Interphases*. 2023;25(2): 257–267. https://doi.org/10.17308/kcmf.2023.25/11106

Research article

https://doi.org/10.17308/kcmf.2023.25/11107

Organic fouling of anion-exchange and bipolar membranes during the separation of amino acid and sucrose by electrodialysis

A. Yu. Kharina, O. E. Charushina, T. V. Eliseeva

Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

The article presents a study of the behaviour of the MA-41 anion-exchange membrane and MB-2 bipolar membrane during the electrodialysis of a solution containing tyrosine and sucrose. It establishes changes in current-voltage, transport, and structural characteristics of ion-exchange membranes. The study of the evolution of membrane characteristics during a prolonged contact with solutions containing an aromatic amino acid and disaccharide is aimed at providing a deeper understanding of and finding solutions to the problem of organic fouling of membranes, which complicates the electromembrane separation of components of the solution during microbiological synthesis of amino acids.

It was found that the fluxes of tyrosine and sucrose through the MA-41 membrane measured after its operation during 50-hour electrodialysis reach higher values than during the first hours of operation after the system reaches a steady state. However, it was noted that when the membrane continues to be used, the flux of components through the MA-41 membrane decreases. What is more, this change is pronounced with a high current density.

This decrease in mass transport, an increased voltage drop on the MB-2 and MA-41 membranes, and lower values for the effective OH ion transport number for the MA-41 membrane are associated with the phenomenon of organic fouling confirmed by revealed structural changes in the ion-exchange material, which become significant after a prolonged contact (more than 60 hours) with a mixed solution of tyrosine and sucrose. These changes are associated with the accumulation of an amino acid and its oxidation product, 3,4-dihydroxyphenylalanine, in the membrane phase, as well as with a decrease in the content of sucrose absorbed by the membrane. **Keywords:** Electrodialysis, Separation, Ion-exchange membrane, Tyrosine, Sucrose, Organic fouling

Funding: The study was supported by the Russian Science Foundation, project No. 22-29-01480.

The IR spectra of the membrane samples were obtained using the equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University. URL: http://ckp.vsu.ru.

For citation: Kharina A. Yu., Charushina O. E., Eliseeva T. V. Organic fouling of anion-exchange and bipolar membranes during the separation of amino acid and sucrose by electrodialysis. *Condensed Matter and Interphases*. 2023;25(2): 268–276. https://doi.org/10.17308/kcmf.2023.25/11107

Research article

https://doi.org/10.17308/kcmf.2023.25/11108

Specifying the structural formula of kaolinite from the Orenburg Region by means of spectroscopic methods A. G. Chetverikova¹, V. N. Makarov¹, O. N. Kanygina¹, M. M. Seregin², E. A. Stroganova¹

¹Orenburg State University,

13 Prospect Pobedy, Orenburg 460018, Russian Federation

²LLC "Lumex-Centrum"

28A Varshavskoe sh., Moscow 117105, Russian Federation

Abstract

Kaolinite certification is necessary when using it as a raw material in the ceramic industry. The kaolin clay deposit discovered in the Orenburg Region in 2018 is presumably the largest in the country. Within the Koskolskaya area, 5 mineral deposits have been described. Three of them are particularly promising deposits of high-quality kaolin clay. Previously, studies of the technological and physical characteristics of clay from this deposit were carried out. The purpose of our study was to derive and specify the structural formula of kaolinite contained in the clays.

After elutriation and grinding in a ball mill, natural clay was sifted through a sieve with meshes of 40 µm. The conducted IR, Raman, and EPR spectroscopy, as well as DTA allowed us to monitor the process of metakaolinisation, which occurs as a result of dehydration of kaolinite (i.e. the process of transformation of kaolinite into metakaolinite). Spectroscopic methods made it possible to analyse the parameters of the fine structure, in particular, the degree of crystallinity of kaolinite particles and the occurrence of iron and magnesium ions in hydroxyl sheets.

Conducting a series of experiments, we managed to specify the structural formula of the kaolinite of the Koskolsky deposit of the Orenburg region:

 $(K,Na,Ca,Ba)_{0.16}$ $Al_{3.62}$ $(Fe^{3+},Fe^{2+})_{0.11}Mg_{0.27}(Mn,Cr)_{0.01}$ $Si_{3.86}Ti_{0.14} O_{10}(OH)_{8}$,

The square brackets indicate the cationic compositions of the hydroxyl and siloxane sheets that formed the surface charge of the mineral particles. Compensator ions remain outside the square brackets. Thus, in our study we assessed the substance used as a raw material in the ceramic industry and determined the role of elutriation and mechanical treatment of kaolin clay.

Keywords: Structure, Kaolinite, XRF spectroscopy, Differential thermal analysis, FTIR spectroscopy, Raman spectroscopy, EPR spectroscopy *Funding:* This study was supported by the Russian Foundation for Basic Research and the government of the Orenburg Region (project No. 9-43-560001 r_a "Physicochemical processes of microwave consolidation of kaolinites").

Acknowledgments: the XRF spectroscopy and the Raman spectroscopy were performed using the equipment of the Engineering Centre of Orenburg State University.

For citation: Chetverikova A. G., Makarov V. N., Kanygina O. N., Seregin M. M., Stroganova E. A. Specifying the structural formula of kaolinite from the Orenburg Region by means of spectroscopic methods. *Condensed Matter and Interphases*. 2023;25(2): 277–291. https://doi.org/10.17308/kcmf.2023.25/11108

Research article

https://doi.org/10.17308/kcmf.2023.25/11168

Phase equilibra in the Ag₂S-Ag₈GeS₆-Ag₈SiS₆ system and some properties of solid solutions

G. M. Ashirov¹, K. N. Babanly¹, L. F. Mashadiyeva¹, Y. A. Yusibov², M. B. Babanly¹

¹Institute of Catalysis and Inorganic Chemistry n.a. M. Nagiyev

113 H. Javid av., Baku Az1143, Azerbaijan

²Ganja State University,

Heydar Aliyev, 187, Ganja AZ2000, Ganja, Azerbaijan

Abstract

Phase equilibria in the $Ag_2S-Ag_8SiS_6-Ag_8GeS_6$ system were studied using differential thermal analysis and powder X-ray diffraction technique. Boundary section $Ag_8SiS_6 - Ag_8GeS_6$, liquidus surface projection, an isothermal section of the phase diagram at 300 K, and some polythermal sections of the studied system were constructed.

The formation of continuous series of solid solutions between both crystalline modifications of the starting compounds was determined in the $Ag_8SiS_6-Ag_8GeS_6$ system. The liquidus surface of the $Ag_2S-Ag_8SiS_6-Ag_8GeS_6$ system consists of two fields corresponding to the primary crystallization of the high-temperature modifications of the HT- $Ag_8Si_{1-x}Ge_xS_6$ and HT- Ag_2S phases. Lattice parameters for both modification of solid solutions were calculated based on powder X-ray diffraction data. The concentration dependence of lattice parameters obeys Vegard's rule. The obtained new phases are of interest as environmentally safe materials with thermoelectric properties and mixed ion-electron conductivity.

Keywords: Argyrodite family compounds, Silver-germanium sulfide, Silver-silicon sulfide, Phase equilibria, Solid solutions, *T-x* diagram, Crystal structure

Acknowledgment: The work was financially supported by the Azerbaijan Science Foundation – Grant No AEF-MCG-2022-1(42)-12/10/4-M-10. *For citation*: Ashirov G. M., Babanly K. N., Mashadiyeva L. F., Yusibov Y. A., Babanly M. B. Phase equilibra in the Ag₂S-Ag₈GeS₆-Ag₈SiS₆ system and some properties of solid solutions. *Condensed Matter and Interphases*. 2023;25(2): 292–301. https://doi.org/10.17308/kcmf.2023.25/11168