Electrical and Optical Properties of Nanocomposites Fabricated by the Introduction of Iodine in Porous Dielectric Matrices

A. I. Vanin^a, Yu. A. Kumzerov^{a, b}, V. G. Solov'ev^{a, c, *}, S. D. Khanin^c, S. E. Gango^a, M. S. Ivanova^a,
M. M. Prokhorenko^a, S. V. Trifonov^a, A. V. Cvetkov^a, and M. V. Yanikov^a

^a Pskov State University, Pskov, 180000 Russia

^b Ioffe Physical-Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia

^c Budennyi Military Academy of the Signal Corps, St. Petersburg, 194064 Russia

*e-mail: solovyev_v55@mail.ru

Received December 8, 2020; revised January 17, 2021; accepted February 5, 2021

Abstract—The electrical and optical properties of nanocomposite materials fabricated by the dispersion of iodine in porous dielectric matrices of zeolites, zeolite-like aluminum phosphates, opals, asbestos, and porous aluminum oxide are studied. It is demonstrated that the physical properties of the produced nanocomposites depend significantly on the structure of a matrix.

Keywords: iodine nanoparticles, matrix nanocomposites

DOI: 10.1134/S1087659621030123

INTRODUCTION

The study of physical phenomena in nanostructures, including phase transitions, is the focus of many researchers. This is explained by the fundamental nature of the problems of physics of low-dimensional systems and the possibilities of the practical application of nanostructures in engineering.

V.N. Bogomolov [1, 2] suggested a matrix method for producing nanostructures, according to which nanoparticles of a guest substance are introduced by various methods into a system of cavities and channels of a porous dielectric host matrix (for example, zeolite or opal) [3, 4]. This method has great potential, allowing us to study ensembles of identical ordered nanoparticles with high concentrations (up to $5 \times 10^{20} \text{ cm}^{-3}$) and ultra-small size (up to 1 nm).

In this study, a hole-type conducting semiconductor iodine was used as the guest substance. It is often considered as the model object when creating and studying various nanostructures in solid-state physics [5–15] and has prospects for practical application in electronics [16], photonics [17], and medicine [18] (where zeolite matrices can be used for targeted drug delivery [19]).

The objective of this study is to compare and analyze the physical properties of iodine nanoparticles in various porous matrices and to study the nature of their effect on the electrical and optical properties of the corresponding nanocomposites.

The porous matrices were made up of framework aluminosilicates: zeolites of type A (Fig. 1a [4]), which have a three-dimensional system of intersecting channels and cavities with the maximum size of 1.14 nm; zeolite-like aluminophosphates of type AFI (Fig. 1b [4]) with quasi-one-dimensional parallel channels with a diameter of 0.73 nm; magnesium hydrosilicate, chrysotile-asbestos (Fig. 1c), containing tubes with an internal diameter of about 5 nm; opals, water-containing silicon oxides of a globular structure (Fig. 1d), the face-centered cubic structure of which include tetrahedral and octahedral cavities (their sizes for the studied samples were about 66 and 120 nm, respectively); and porous aluminum oxide (PAO) with the average pore diameter of 55 nm.

EXPERIMENTAL

The objects of research in this study were nanocomposite materials I/AFI, I/A, I/opal, I/asbestos, and I/POA fabricated by heating the samples of porous dielectric matrices (zeolite-like aluminum phosphate type AFI, zeolite type A, opal, asbestos, and porous aluminum oxide, respectively) in evacuated ampoules in iodine vapor at temperatures of 580 to 775 K and a partial pressure of iodine vapor ranging from 3.5 to 7.0 atm for 6–12 h. Structural studies [7, 11, 15] show that, under these conditions, iodine nanoparticles are formed in cavities and channels of porous dielectric matrices.

Fig. 1. Models of structures of porous dielectric matrices: zeolite A(a), zeolite-like aluminum phosphate AFI (b), asbestos (c), opal (d).

Polycrystalline samples for electrical measurements were fabricated as follows. Microcrystals of zeolite type A were compacted using a hydraulic press at a pressure of 100 MPa into tablets of a diameter of 10 mm and a thickness of 1 mm with a binder (potassium bromide), the weight of which ranged from 50 to 90% of the weight of a tablet. The electrophysical characteristics of the polycrystalline samples with graphite electrodes in alternating current were measured using an E7-13 RLC meter at a frequency of 1 kHz with a parallel substitution circuit, whereas in direct current, measurements were taken using an M-95 microammeter, as well as SP-1M Cactus and Keithley 6517B electrometers. The temperature dependences of the conductivity and capacitance were studied under continuous heating or cooling of a sample at a rate of 1 to 2 K/min.

Special experimental techniques described in detail in [4, 10] were used to study the electrical and thermoelectric properties of the microsamples.

The optical properties of the I/opal and I/POA samples were studied by the Bragg spectroscopy and spectral ellipsometry using experimental installations based on a USB650 Red Tide spectrometer and an Ellipse-1891 spectroellipsometer. The diffusion reflection spectra of zeolite powders $R_d(\lambda)$ were measured by the standard method using an SF-16 spectrophotometer with a PDO-1 diffusion reflection accessory in the wavelength range from 220 to 1200 nm. Magnesium oxide was used as the reference. The optical absorption of the samples in relative units was calculated from the diffuse reflection spectra of the powders using the traditional Gurevich–Kubelka–Munk function [20, 21]:

$$F(R_d) = \frac{(1 - R_d)^2}{2R_d}.$$

RESULTS AND DISCUSSION

As the experiment shows, the introduction of iodine nanoparticles in the quasi-one-dimensional channels of the AFI dielectric matrix [22] results in the increase of the conductivity of the samples, as well as

in the decrease in the specific thermo-EMF of the nanocomposite I/AFI and changes in its sign compared to the Seebeck coefficient of the bulk iodine, which may be related to the transition of iodine to the ultradispersed state [10, 13].

As a result of the introduction of iodine, the initially transparent AFI single crystals acquire a brown color, thus demonstrating optical anisotropy in polarized light, which indicates the formation of iodine chains in the quasi-one-dimensional channels of the AFI single crystals [7, 10]. Anisotropy is also revealed in the electrical properties of the I/AFI samples: the nature of the temperature dependences of the conductivity differs in two directions: parallel and perpendicular to the optical axis of an AFI single crystal. Here, in the first case, when the I/AFI sample is heated, a posistor effect is detected: it is determined by the phase transition at a temperature of ~ 343 K in the subsystem of iodine nanoparticles (Fig. 2, curve 1), which is related to the decomposition of iodine chains into molecular fragments in the channels of the AFI matrix [7, 11]. When the I/AFI nanocomposite (Fig. 2, curve 2) heated to a temperature $T > 343$ K is cooled, the temperature hysteresis is observed (it takes a certain amount of time for the reformation of iodine chains in the narrow quasi-one-dimensional channels of the AFI matrix). Similar, albeit, less pronounced, effects were observed in the I/PAO [12] and I/A [13] samples.

When iodine is introduced into the channels of the asbestos matrix, the diameter of which is an order of magnitude larger than that of the channels of the AFI matrix [22, 23], the temperature dependence of the conductivity of the obtained samples is significantly different. With the temperature increasing, it decreases at first, and when the temperature reaches 343–353 K, it starts to increase. During cooling, the nature of the process is repeated (Fig. 2, curves 3, 4). During repeated heating and cooling, the minimum current strength is shifted to the low-temperature region, presumably due to the release of iodine from the asbestos channels. The different nature of the temperature dependences of the conductivity of the I/AFI and I/asbestos samples can be related to the fact that, in the narrow channel of the AFI matrix, iodine forms

Fig. 2. Temperature dependences of the current at constant voltage along the channels of the samples I/AFI (1, 2) and I/asbestos (3, 4) when heated (1, 3) and cooled (2, 4).

only one quasi-one-dimensional chain. Multiple quasi-one-dimensional chains of iodine are formed in a wide channel of the chrysotile-asbestos matrix. With the increase of the temperature of the I/asbestos sample, the thermal oscillation of the iodine chains create additional obstacles to the movement of the conduction electrons along the chains, which leads to a decrease in the conductivity. In the I/asbestos nanocomposite, the iodine molecules in each channel are surrounded by many neighbors, so that the breakdown of the chains does not lead to a break in the electrical circuit (as in the I/AFI nanocomposite), but only to a change in the current flow paths. As the experiment shows (Fig. 2), and the chain will probably be restored during the cooling of the I/asbestos sample.

In addition to the observed changes in the color of the samples and the anisotropy of the optical transmission of the I/AFI samples, as a result of the introduction of iodine into type A zeolites, a size effect is observed in the diffusion reflection spectra of the I/A nanocomposites during the transition of iodine to the ultradispersed state. As Fig. 3, curve 1 [13] shows, the initial zeolite matrix is transparent in the investigated spectral range. The absorption edge of the bulk guest substance (Fig. 3, curve 2) is in close agreement with the value of the band gap of crystalline iodine (~ 1.25 eV). The absorption spectrum of the I/A nanocomposite sample (Fig. 3, curve 3) shows a significant “blue”

shift of the absorption edge in comparison with the corresponding spectrum of bulk iodine, due to the quantum size effect, and three absorption bands with maxima near 2.70, 3.44, and 4.13 eV correlating to the absorption lines of molecular iodine.

The dimensions of the cavities in the opal matrices [24] are 2 orders of magnitude larger than the corresponding values for the pores of zeolites, and therefore the nanocomposite I/opal is unstable (a volatile substance, iodine quickly exits the opal cavities). As can be seen from the reflection spectra of the initial opal and the freshly prepared I/opal sample (Fig. 4 [17]), the introduction of iodine nanoparticles into the opal leads to a noticeable shift in the maxima of the Bragg reflection of the photonic crystal in the “red” region, and, due to the uneven distribution of iodine in the opal, a weaker band characteristic of the initial opal matrix is also present in the spectrum. The ellipsometric measurements corroborate the increase of the effective refractive index of the I/opal nanocomposite in comparison with the refractive index of the original opal matrix.

CONCLUSIONS

When iodine is introduced into silicate and the related dielectric matrices, this guest substance can affect the physical properties of the resulting nano-

Fig. 3. Graphs of the Gurevich-Kubelka-Munk function $F(R_d) = \frac{(1 - R_d)^2}{2R_d}$ based on the diffuse reflection spectra of the zeolite powders of type A (1), bulk iodine (2), and nanocomposite I/A (3).

Fig. 4. Normalized reflection spectra of the initial matrix of opal (1, 2) and nanocomposite I/opal (3, 4) at the angles of incidence of light 15° (1, 3) and 30° (2, 4).

composites in different ways, which is largely determined by the structural features of the host matrix. The nature of the temperature dependence of the conductivity of the nanocomposite obtained by the introduction of iodine nanoparticles into the channel dielectric matrix depends significantly on the diameter of the channels. The optical properties of iodine nanoparticles introduced into regular porous matrices reveal a quantum size effect, as well as the effect of the guest substance on the Bragg diffraction of light in photonic crystal structures.

ACKNOWLEDGMENTS

The authors thank N.O. Alekseeva, V.L. Veisman, V.I. Gerbreder, A.S. Ogurcov, A.E. Lukin, and M.I. Samoilovich for providing the samples for research, assistance in conducting experiments, and their useful discussions.

FUNDING

The study was partially supported by the Russian Foundation for Basic Research (RFBR) as part of project no. 20-32-90003.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

OPEN ACCESS

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

REFERENCES

1. Bogomolov, V.N., Fluids in ultrathin channels (filament and cluster crystals), *Sov. Phys. Usp.*, 1978, vol. 21, no. 1, pp. 77–83.
2. Astratov, V.N., Bogomolov, V.N., Kaplyanskii, A.A., Prokofiev, A.V., Samoilovich, L.A., Samoilovich, S.M., and Vlasov, Yu.A., Optical spectroscopy of opal matrices with CdS embedded in its pores: Quantum confinement and photonic band gap effects, *Nuovo Cim., Soc. Ital. Fis., A*, 1995, vol. 17D, nos. 11–12, pp. 1349–1354.
3. Kumzerov, Y. and Vakhrushev, S., Nanostructures within porous materials, in *Encyclopedia of Nanoscience and Nanotechnology*, Nalwa, H.S., Ed., Am. Sci., 2004, vol. 7, pp. 811–849.
4. Solovyev, V.G., Ivanova, M.S., Pan'kova, S.V., Trifonov, S.V., and Veisman, V.L., Preparation and physical properties of zeolite, zeolite-like single crystals and zeolite-based nanocomposite materials, in *Handbook of Zeolites: Structure, Properties and Applications*, Wong, T.W., Ed., New York: Nova Science, 2009, chap. 5, pp. 77–79.
5. Zhou, W., Xie, S., Sun, L., Tang, D., Li, Y., Liu, Z., Ci, L., Zou, X., Wang, G., Tan, P., Dong, X., Xu, B., and Zhao, B., Raman scattering and thermogravimetric analysis of iodine-doped multiwall carbon nanotubes, *Appl. Phys. Lett.*, 2002, vol. 80, no. 14, pp. 2553–2555.
6. Flachenecker, G. and Materny, A., The elementary steps of the photodissociation and recombination reactions of iodine molecules enclosed in cages and channels of zeolite crystals: A femtosecond time-resolved study of the geometry effect, *J. Chem. Phys.*, 2004, vol. 120, no. 12, pp. 5674–5690.
7. Ye, J.T., Tang, Z.K., and Siu, G.G., Optical characterizations of iodine molecular wires formed inside the one-dimensional channels of an $\text{AlPO}_4\text{-5}$ single crystal, *Appl. Phys. Lett.*, 2006, vol. 88, pp. 073114-1–073114-3.
8. Jiang, F.Y. and Liu, R.C., Incorporation of iodine into the channels of $\text{AlPO}_4\text{-5}$ crystals, *J. Phys. Chem. Solids*, 2007, vol. 68, no. 8, pp. 1552–1555.
9. Zhai, J.P., Lee, H.F., Li, I.L., Ruan, S.C., and Tang, Z.K., Synthesis and characterization of iodine molecular wires in channels of zeolite ael single crystals, *Nanotechnology*, 2008, vol. 19, pp. 175604-1–5.
10. Trifonov, S.V., Vanin, A.I., Veisman, V.L., Gango, S.E., Kondrat'eva, M.N., and Solov'ev, V.G., Experimental investigation into electrophysical properties of microscopic samples of I/AFI nanocomposites, *Nanotekhnika*, 2011, no. 2, pp. 78–82.
11. Ye, J.T., Iwasa, Y., and Tang, Z.K., Thermal variations of iodine nanostructures inside the channels of $\text{AlPO}_4\text{-5}$ zeolite single crystals, *Phys. Rev. B*, 2011, vol. 83, no. 19, pp. 193409-1–4.
12. Alexeeva, N., Cema, G., Podorozhkin, D., Solovyev, V., Trifonov, S., and Veisman, V., Physical properties of self-assembled porous alumina structures filled with iodine, *J. Self-Assembly Mol. Electron.*, 2015, vol. 2, pp. 27–40.
13. Cvetkov, A.V., Gango, S.E., Ivanova, M.S., Khanin, S.D., Lukin, A.E., Solovyev, V.G., Trifonov, S.V., and Veisman, V.L., Electrical and optical properties of iodide nanoparticles embedded into zeolite porous matrices, *J. Phys.: Conf. Ser.*, 2017, vol. 929, pp. 012042-1–012042-6.
14. Qiu, L., Zou, H., Zhu, N., and Feng, Y., Zhang, X., Zhang, X.-X., Iodine nanoparticle-enhancing electrical and thermal transport for carbon nanotube fibers, *Appl. Therm. Eng.*, 2018, vol. 141, pp. 913–920.
15. Chen, S., Li, X., Yao, Z., Lv, H., Dong, E., Yang, X., Liu, R., and Liu, B., High temperature driven transformation of iodine species in AFI and AEL channels: A comparative study, *Microporous Mesoporous Mater.*, 2019, vol. 290, pp. 109682-1–7.

16. Khanin, S., Solovyev, V., Trifonov, S., and Veisman, V., Phase and structure transitions in nanoparticles of semiconductors within porous dielectric matrices, *Smart Nanocomposites*, 2013, vol. 4, no. 1, pp. 29–36.
17. Yanikov, M.V., Veisman, V.L., Gonyan, A.A., Solov'ev, V.G., and Tsema, G.S., Preparation and experimental investigation onto optical properties of nanostructures iodide in opar porous matrix, *Vestn. Pskov. Univ., Ser.: Estestv. Fiz.-Mat. Nauki*, 2013, no. 3, pp. 165–169.
18. Hainfeld, J.F., Ridwan, S.M., Stanishevskiy, Y., Smilowitz, N.R., Davis, J., and Smilowitz, H.M., Small, long blood half-life iodine nanoparticle for vascular and tumor imaging, *Sci. Rep.*, 2018, vol. 8, pp. 13803-1–13803-10.
19. Golubeva, O.Yu., Brazovskaya, E.Yu., Alikina, Yu.A., D'yachenko, S.V., and Zhernovoi, A.I., Synthesis and study of nanocomposites based on beta zeolite and magnetite for targeted drug delivery, *Glass Phys. Chem.*, 2019, vol. 45, no. 1, pp. 66–73.
20. Gurevič, M., Über eine rationelle Klassifikation der Lichtstreuenden Medien, *Phys. Zeitschr.*, 1930, vol. 31, pp. 753–763.
21. Kubelka, P. and Munk, F., Ein Beitrag zur Optik der Farbanstriche, *Zeitschr. Tech. Phys.*, 1931, vol. 12, no. 11a, pp. 593–601.
22. Trifonov, S.V., Ivanova, M.S., Markov, V.N., Pan'kova, S.V., Veisman, V.L., and Solov'ev, V.G., Synthesis and physical properties of single crystals of zeolite-like aluminophosphates of the AFI type, *Glass Phys. Chem.*, 2007, vol. 33, no. 3, pp. 259–261.
23. Belotitskii, V.I., Kumzerov, Yu.A., Kalmykov, A.E., Kirilenko, D.A., Peschel, U., Romanov, S.G., Sorokin, L.M., Sysoeva, A.A., and Zhuromskyy, O., Optical properties of metal nanoparticles in chrysotile channels, *Tech. Phys. Lett.*, 2016, vol. 42, no. 12, pp. 656–658.
24. Balakirev, V.G., Bogomolov, V.N., Zhuravlev, V.V., Kumzerov, Yu.A., Petranovskii, V.P., Romanov, S.G., and Samoilovich, L.A., Three-dimensional superlattices in opal matrices, *Crystallogr. Rep.*, 1993, vol. 38, no. 3, pp. 348–353.

Translated by D. Marinin