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Properties of nanodimensional silicon dioxide modified with silver iodide

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The electrophysical and thermophysical properties of nanodimensional silica modified by silver iodide have been studied. We have shown that chemical modification of silica surface by AgI allows one to extend the range of controlled variation of complex dielectric constant values for the AgI–SiO2 system and optimize its practical application in manufacturing of materials that efficiently interact with electromagnetic radiation.

Key words: nanodimensional silicon, superionic conduction, phase transition, complex permittivity, thermal capacity, percolation threshold.

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Introduction

Creation of novel functional materials with preassigned and adjustable characteristics is an acute problem. Such materials may be designed using modified forms of nanodimensional silicon dioxide (SiO_2). The major procedure for varying the nature of a disperse silica surface with a view to impart new properties to the material obtained involves chemical modification that makes it possible to develop cluster structures of diverse configurations [1].

Our analysis of results of researches performed in this country and abroad gives evidence for the fact that ionic and molecular crystals may be promising components of heterogeneous systems. At interfaces of ionic crystals in such systems there are double electrical layers whose charge and potential exert a substantial effect on interphase interactions which lead to changes in the structure and in thermodynamic, electrophysical, and chemical properties. Thus, composites of the type 'ionic salt–oxide' may have much promise for designing supermolecular solid electrolytes [2] that are completely confined to the region of interphase contacts. The confinement, in its turn, results in efficient interphase interactions. An interface in such systems can possess characteristics which are not inherent in individual constituents and, thereby, make a considerable contribution to the composite properties [3].

The authors of Refs. [4,5] observed a number of new specific effects and phenomena in a dispersion-filled system with polychlorotrifluoroethylene (PCTFE) as a polymeric constituent. For instance, in the system PCTFE – AgI-SiO_2 such effects and phenomena are consequences of physic-chemical interactions at the phase interface. In particular, introduction of highly disperse silica into composites PCTFE – AgI brings about an increase in their electrical conductivity and permittivity as well as a shift in their percolation threshold into a region with a lower silver iodide content.

This work was intended to study electro- and thermophysical properties of disperse systems on the basis of nanodimensional silicon dioxide as a function of AgI content in a wide interval of temperatures.

I. Synthesis and identification materials

The samples necessary for the studies were prepared by a chemical method for modifying silica with silver iodide during the course of release of AgI from an aqueous solution of $AgNO_3$ and KI in the presence of SiO_2 to obtain modified silica (MS) or by a physical method for mechanical mixing of ingredients AgI and SiO_2 to obtain a physical mixture (PM). Before the X-ray diffraction procedure the samples were compacted at a pressure of 1 MPa at room temperature. Diffractograms for samples of MS (Fig. 1) were recorded on a diffractometer DRON-4-07 using CuK_α radiation of an anode with a nickel filter in the reflected beam mode and the Bragg-Brentano geometry.

Our identification of the observed diffraction maximums provides evidence for the fact that in all the samples of MS there is a hexagonal modification of silver iodide. Besides, it is seen that the major reflection

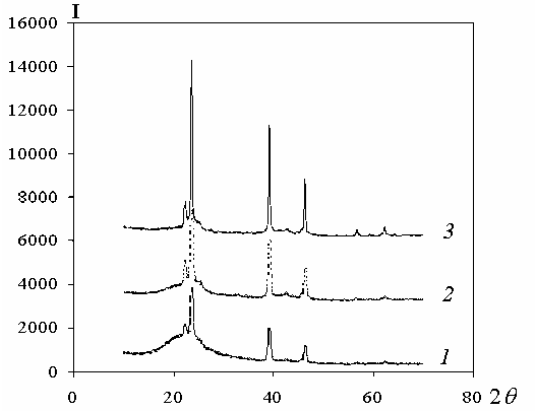

Fig. 1. Diffractograms for samples of nanodimensional silicon dioxide modified with silver iodide at various concentrations of AgI (in wt %). *1*– 4.7; *2* – 16.6; *3* – 48.7.

intensity increases in proportion to the content of AgI in the samples. The diffuse halo in the range of 2θ = 22° is attributed to silicon dioxide. The average size of AgI crystallites was determined in terms of the most intense line of AgI, namely for (002), according to the Scherer equation $d = k\lambda/\beta \cos\theta$ [6]. The calculation results indicate that with increasing silver iodide content in MS from 2.4 to 48.7 wt % the crystallite size d increases from 30 to 45 nm.

II. Results and discussion

The results of our measurements of the thermal capacity (C_p) for samples of MS at various contents of AgI are illustrated in Fig. 2. It is seen that with increasing

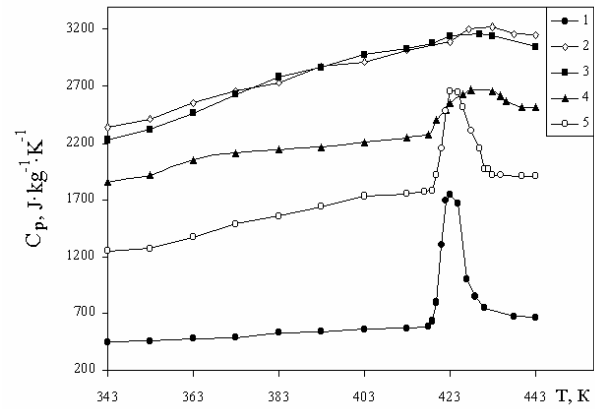

Fig. 2. Temperature dependence of C_p for ultradisperse SiO_2 modified with AgI at its various contents (in wt %). 1 – 100; 2 – 2.5; 3 – 9.0; 4 – 16.6; 5 – 33.3.

content of silver iodide C_p decreases. At a temperature of 420 K for a pure AgI sample (curve 1) its thermal capacity values show a maximum, which corresponds with phase transition $\beta \rightarrow \alpha$. The same character of dependence $C_p = f(T)$ is observed for sample 5, with its higher thermal capacity values being attributed to higher contents of silicon dioxide in the system. Diffuse

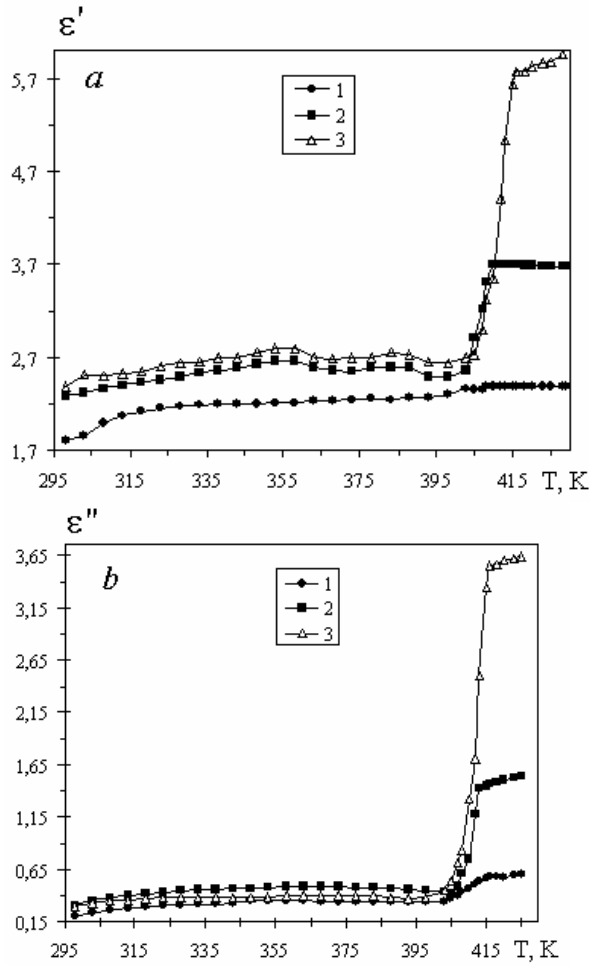

Fig. 3. Temperature dependence of real component ε' (*a*) and imaginary component ε'' (b) of the complex permittivity for nanodimensional SiO_2 modified with silver iodide at various concentrations of AgI (in wt %). 1 – 16.6; 2 – 33.3; 3 – 48.7.

maximums of curves 2–4 are assigned to an effective interaction between SiO_2 and AgI.

With the help of a superfrequency interferometer (operated in the wave mode at a frequency of 8-12 GHz) a research has been made into complex permittivity [7]. The dependence of real component ε' (a) and imaginary component ε'' (b) of the complex permittivity for samples of MS is displayed in Fig. 3. From the data presented it is evident that at a temperature of 420 K one can observe a sharp increase in the ε' and ε'' values as a result of a transition of silver iodide to the superionic state [8].

The comparison of temperature dependences of permittivity for MS and PM (Fig. 4) shows that at T > 420 K the corresponding values of ε' and ε'' differs greatly (by a factor of 1.5 and 10, respectively). As it has been shown by the electron microscopy studies, modification of the surface of nanodimensional silica leads to a decrease in size of AgI particles from 4-6 μm to 0.6-1.0 μm (for PM) (Fig. 5) and to formation of more ramified clusters. They are distinguished for a more effective interaction with electromagnetic radiation, which is evidenced for by the results of the researches into permittivity for MS and PM in the case of the system

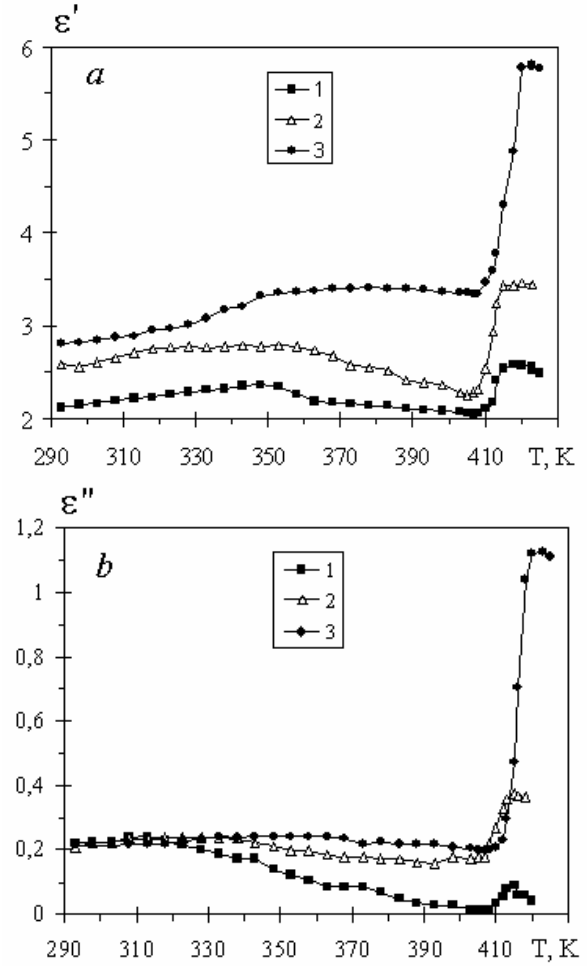

Fig. 4. Temperature dependences of real (*a*) and imaginary (*b*) components of complex permittivity for the physical mixture SiO_2-AgI at various concentrations of AgI (in wt %). 1 – 33.3; 2 – 48.7; 3 –70.0.

AgI-SiO_2 (Fig. 6).

A study has also been made of the dependence of real and imaginary components of complex permittivity on content of AgI for the MS system. The results achieved show that beginning from the content C = 20 wt % one can observe a sharp increase in the ε′ and ε″ values (Fig. 6).

The character of the observed changes shows that in the MS system there proceeds a percolation transition 'system of isolated clusters → infinitely great cluster', with the critical percolation threshold being attained at about 20 wt % of AgI. In the case of the composites prepared by the method for mechanical mixing of ingredients the percolation threshold is observed at a higher content of AgI (at about 60 wt %).

Conclusions

Thus, when analysing the experimental study results it is possible to draw a conclusion that due to interphase

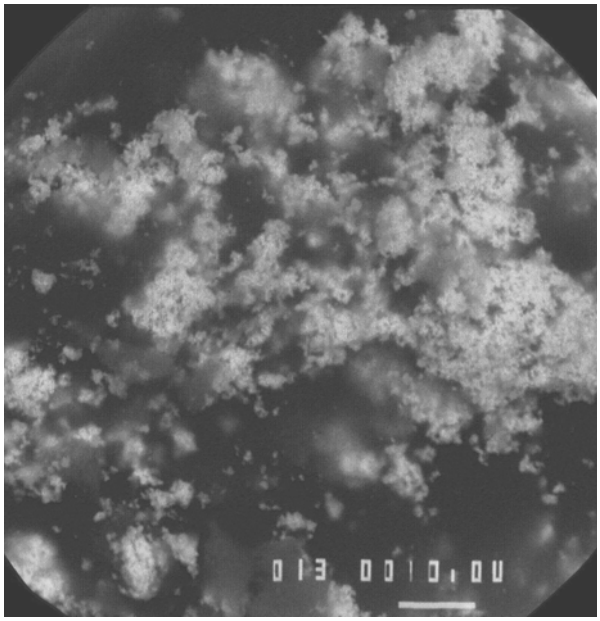

Fig. 5. Electron micrograph of a silica sample modified with silver iodide at its content of 48.7 wt %.

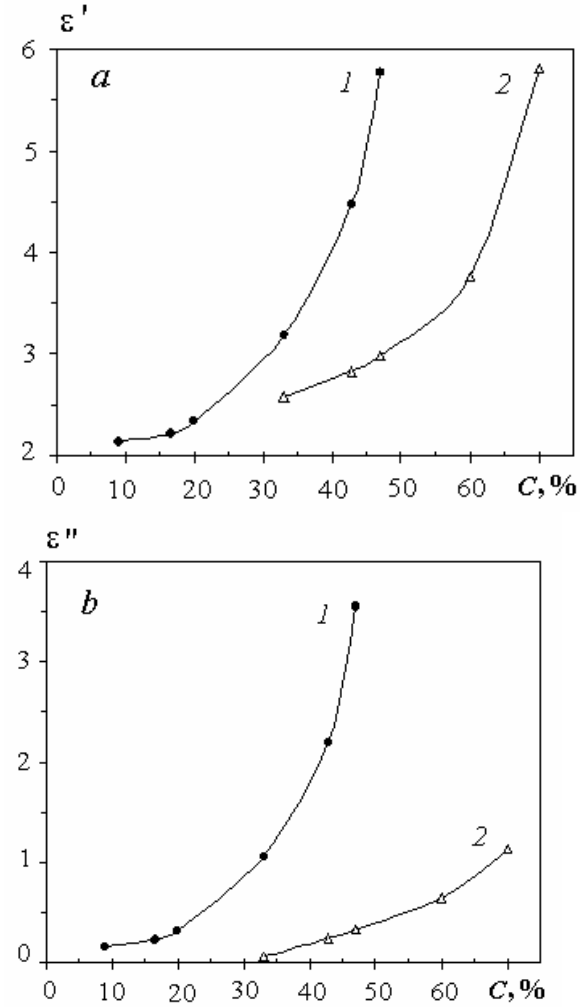

Fig. 6. Dependence of real (a) and imaginary (b) components of complex permittivity on content of AgI (C) for the systems under consideration. 1: nanodimensional silicon dioxide modified with silver iodide; 2: physical mixture AgI–SiO_2.

interactions involving nanodimensional silica modified with silver iodide there appears a system of clusters which is more ramified than that observed in PM. As a consequence, the percolation threshold turns out to be smaller (by a factor of ~ 3), while the dielectric loss becomes substantially higher. The surface modification allows one to enlarge the interval of controlled changes in the complex permittivity values attainable for the system AgI–SiO_2, which offers ample scope for application of the system as an active component of materials which are distinguished for their efficient interactions with electromagnetic radiation.

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Властивості нанорозмірного діоксиду кремнію, модифікованого йодидом срібла

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Досліджено електрофізичні та теплофізичні властивості нанорозмірного кремнезему, модифікованого йодидом срібла. Показано, що хімічна модифікація поверхні кремнезему AgI дозволяє розширити діапазон керованої зміни значень комплексної діелектричної проникності системи AgI–SiO_2 та оптимізувати її практичне використання з метою виготовлення матеріалів, що ефективно взаємодіють з електромагнітним випромінюванням.

Ключові слова: нанорозмірний діоксид кремнію, суперіонний провідник, фазовий перехід, комплексна діелектрична проникність, теплоємність, поріг перколяції.