INVESTIGATION OF NANOPOWDER DISPERSED SYSTEM BASED ON ZIRCONIA BY TRANSMISSION ELECTRON MICROSCOPY, ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AND SPIN-ECHO

ИССЛЕДОВАНИЕ НАНОПОРОШКОВОЙ СИСТЕМЫ НА ОСНОВЕ ZrO2 МЕТОДАМИ ЭЛЕКТРОННОЙ МИКРОСКОПИИ, ИМПЕДАНСНОЙ И И СПИНОВОГО ЭХА

Doroshkevich A.S.[1,2], Shylo A.V.[1], Lyubchyk A.I.[3] Kirillov A.K.[4], Glazunova V.A.[7], Zelenyak T.Yu.[5], Burkhovetskiy V.V[7], Troitskiy G.A.[4], Vasilenko T.A.[3], Bacherikov Yu.Yu. [6], Sinyakina S.A.[2], Akhkozov L.A.[2], Turchenko V.A.[1,2], Bodnarchuk V.I.[2],. Doroshkevich V.S.[8], Kholmurodov Kh.T.[2], Konstantinova T.E.[1]

Donetsk Institute for Physics and Engineering NAS of Ukraine, 03680, Nauki ave, 46, Kyiv, Ukraine[1]
Joint Institute for Nuclear Research, 141980, str. Joliot-Curie, 6, Dubna, Russia[2],
REQUIMTE, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal [3]
Institute of Physics of Mining Processes, NAS of Ukraine, 49005, st. Simferopol, 15, Dnepropetrovsk, Ukraine[4]
Dubna International University for Nature, Society and Man, 141980, st. Universitetskay, 19, Dubna, Moscow region, Russia[5]
Institute of Semiconductor Physics V.E. Loshkareva NAS of Ukraine, 03028, Nauki ave, 41, Kiev, Ukraine[6]
Donetsk Institute for Physics and Engineering, 83114, R. Luxembourg str., 72, Donetsk, Ukraine[7]
Donetsk National University, Shchorsa str., 17-a, 83001 Donetsk, Ukraine[8]

Abstract: *A comprehensive study of the structure and electrical properties of nanopowder system based ZrO_2 + Y_2O_3 3mol% was conducted. The presence of electrically continuous ion atmosphere, which consist from hydrogen-containing functional groups with different spin-spin relaxation times of hydrogen nuclei 1H was revealed. An original method of investigation of electrical properties of nanoparticles and surrounding ionic atmosphere based on electrochemical impedance spectroscopy was suggested.*

KEYWORDS: *NANOPOWDER, NANOTECHNOLOGY, ELECTRICAL DOUBLE LAYER, DIMENSIONAL EFFECTS*

1. Introduction

Nanomaterials based on zirconia present a great interest for modern science and technology due to their special properties associated with size effects [1, 2, 3, 4]. ZrO_2 nanopowders are excellent sorbents [5], have unique spectral characteristics [6] and promising as a material for the creation of a new generation of phosphors, devices for photovoltaics, electronics [7, 8] and energy [9,10].Reducing of grain size leads to stabilization of tetragonal phase during hardening transformation of ZrO_2 - ceramic [11] and to significant increasing of physical and mechanical and performance characteristics of ceramic products.

Recently, global problem of creating of new alternative power sources became topical [12].Zirconia is a wide-gap insulator (bandgap = 3,5 ÷ 6eV) and differs from other oxides by relatively high value of dielectric constant (ε = 25) and high chemical activity of the surface. Therefore, on high heterophase boundary of nanostructured media based on ZrO_2 a high density of energy can be expected. This is caused interest for their application as functional materials for devices for electronics, energy, and other fields of science and technology [13, 14].

However, due to lack of knowledge about nanopowder systems, dimensional effects caused by excess surface energy in nanopowder systems are the source of most serious technological problems. In particular, inability to overcome the effects of adhesion of nanoparticles causing the problem for obtaining products with complex forms from nanostructured ceramic based on ZrO_2 [15, 16, 17]. Problem of tunnel leakage current at scaling in low-dimensional range of devices for electronics held back the development of microsystems technology and modern electronics as a whole [18].

The spatial structure of nanosized dispersed system, electrical properties, mechanisms of formation and retention of adsorption equilibrium has not been fully explored due to complexity of the object of research and lack of research methods. Topical is not only the study of nanopowder systems, but the development of appropriate methodology for such investigations.

The aim of this study was a comprehensive study of the structure and electrical properties of the nanopowder system based on ZrO_2 by electron microscopy, electrochemical impedance spectroscopy (EIS), spin echo of wide lines based on nuclear magnetic resonance(NMR).

2. Experimental Procedure

As the object of investigation compact sets in the form of tablets (hight - 2mm, diameter - 18mm), obtained by influence of high hydrostatic pressure (HHP, 500 MPa) of ZrO_2-3mol.% Y_2O_3 nanopowder. These nanopowders were prepared by co-precipitation method from salts of zirconia and yttria with ammonia, followed by dehydration of sludge in specialized microwave oven and heat treatment at T = 700°C for 2h.

Spatial structural organization of samples were investigated by scanning (SEM) and transmission (TEM) electron microscopy [19] using JSM640LV and JEM 200A devices respectively.

Electrochemical impedance spectra of samples were obtained using a virtual analyzer of impedance parameters such as impedance Z-1500J, with a computer-controlled process of measurement and recording of experiment results. The amplitude of the signal voltage was 50 mV, the measurement time of each point 5 seconds, automatic switching of measuring range, frequency range from 500 Hz to 1 MHz. The measurements were carried out at temperature of +20°C and atmospheric pressure. Spectra modeling was performed using the computer program published in [20]. Carbon contacts received by mechanical application of graphite to the ends of the samples - tablets.

Analysis of adsorption layer was performed using NMR spectrometer by spin-echo of broad lines technique, operates at 20 MHz (resonant frequency of hydrogen nuclei ^{1}H). Sample for this method amounted to 0.9 g.

3. Results and discussion

3.1. Investigation of nanoparticles morphology and microstructure of the samples – compact sets

Investigation of composition of the powder ZrO_2+3mol% Y_2O_3, (700°C, 2h) by TEM methods are shown on Figure 1. It

can be seen that the powder is relatively well distributed spatially with individualized particles (Figure 1, b). The volume of the sample contains only solid nanoparticles with diameter 20 nm, and the gas phase. Shells around the particles are visible on Figure 1, b. It is formed as a result of contamination of the surface of nanoparticles of pairs of vacuum oil. This item directly indicates high chemical activity of nanoparticles and can indirectly indicate the presence on surface of nanoparticles of adsorption atmosphere, which probably does not create an electronic contrast and not visible in TEM images. The diffraction pattern (Figure 1, c) corresponds to tetragonal zirconia.

Homogeneous microstructure can be seen on SEM images with magnification x500 (Figure 2, a). It is indicates a relatively homogeneous distribution of the material in the volume of samples. At higher magnification pores which are occupied on average half of the sample volume and facilitate easy penetration of moisture are visible. Image with magnification x10 000 shows that microstructure of sample is loose and flake. Aggregates are irregular in shape; their size is 1 - 3mkm.

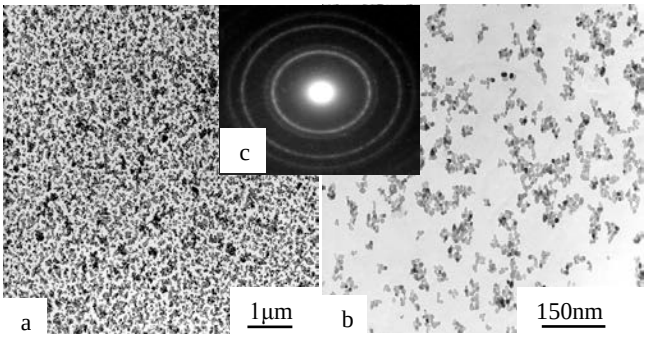

Figure 1. TEM images of the powder ZrO_2 + 3 mol.% Y_2O_3, (700°C, 2h) with magnification of 10 000 (a) 70 000 (b) and the characteristic pattern of the electron diffraction (c).

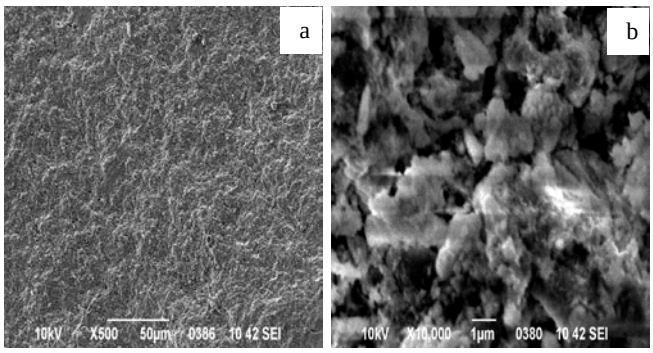

Figure 2. SEM images of fracture of compact sets (500 MPa) of the powder ZrO_2 + 3mol.% Y_2O_3 (700°C, 2h) with magnification of 500 (a) and 10 000 (b).

3.2. Investigation of electrical properties of samples

Hodograpf obtained by mathematical processing of frequency dependence of capacitance, conductivity, and loss tangent of samples is shown on Figure 3. It is contains information about electrical structure of the object.

Presence of several geometric shapes on the hodograph (Figure 3, a) indicates that the sample space is heterogeneous towards to electrical properties.

Figure 3, b shows simulated equivalent circuit diagram of measured sample. It is seen that a typical hodograph can be approximated in the form of two series-connected parallel RC - circuits.

For a more accurate approximation capacitive element C in both circuits is replaced by a so-called constant phase element (CPE). The impedance of this element is given by the formula: $Z_{CPE}(i\omega) = A^{-1}(i\omega)^{-n}$, where A - the coefficient of proportionality, and the n - exponent that characterizes the phase shift [21]. Calculated values of elements shown in Table 1 below.

Circuit R_1-CPE_1 appropriate to located in high frequency part of the spectrum semicircle α (Figure 3, a) with an offset to the center of negative values. It reflects the total conductivity of structural elements with short relaxation times τ_{hf}. Circuit R_2-CPE_2 corresponds to the straight region γ in the low frequency range. It reflects the total conductivity of the structural elements with large relaxation times τ_{lf}.

Table 1. Estimated values of elements of equivalent circuit of the hodograph.

R_1, Ohm	1.53e+6
R_2, Ohm	95944
P_1	4.78e-9
n_1	0.97
P_2	5.09e-10
n_2	0.79
L_1, Hn	9.53e-13

If it is assumed that elements with different own relaxation times τ_{hf} τ_{lf} spatially separated, the system can be represented in the form of spatial domains / layers ordered by frequency / time response τ (principle partial linear approximation [20]). Assuming the spatial symmetry towards to electrical properties, the system under study can be represented schematically as on Figure 2, a, and their electrical properties can be characterized from the shape of corresponding elements of the hodograph. The shape of the spectrum in the form of a semicircle indicates capacitive conductivity of corresponding spatial region, the shape of the beam – diffusion conductivity.

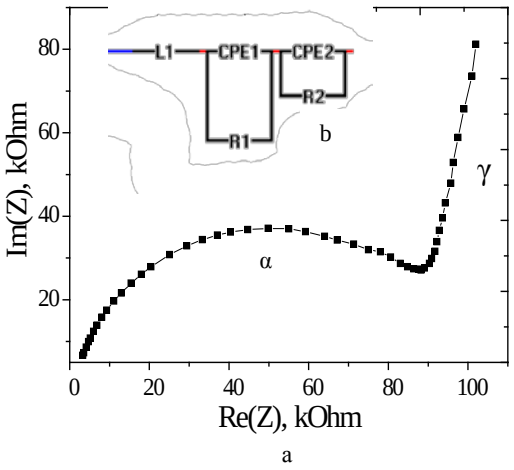

Figure 3. Hodograph of impedance of sample composition ZrO_2-3 % Y_2O_3 (700 °C, 2h)

3.3. Spatial configuration of the system

Area with capacitive conductivity, which for some value τ_s goes to the diffusion conductivity [22, 23, 24] γ, located at the beginning of the reaction coordinate axis, is shown as a circle on Figure 4, a. Based on electron microscopy data, it is possible to assume that part of the spectrum α (Figure 4, b) with capacitive conductivity and typical for diffusion-free (polarization processes), low own relaxation times τ_{hf} characterizes volume of dielectric nanoparticles of ZrO_2.

In this case a straight beam γ (Figure 3, a, Figure 4, b) with the own time τ_{lf} must match the spatial region between the particles and transitional area between the semi-circle and the

line - heterophase boundary. Other components, as shown by TEM- method, are absent in the system.

Thus, the spatial structure of the sample represented in the form of Figure 4, c. Such representation is typical for systems with a liquid electrolyte, for example, cell lithium-ion batteries [22, 23]. Thus, the geometric image of the system under study, obtained from EIS spectra corresponds to the simplest spatial of dispersed system in a packed (concentrated) form, which is confirmed by electron microscopy. Note that the semicircle α is asymmetric. In fact, the low-frequency region is planned plateau of direct current conductivity - frequency independent region that is associated with the formation of the space charge on heterophase boundary [24]. Thus, it can be assumed that the surface of nanoparticles is charged.

3.4. The structure of the hydrate layer

Results of the study of the spin-echo method are shown on Figure 5. NMR spectroscopy technique used two-pulse method, which envisages changes in the pulse frequency υ [25, 26]. For calculation of time T_2 relaxation curves of the magnetic moment of the hydrogen nuclei by transformation $\tau = 1/\upsilon$ were transferred from frequency to time domain.

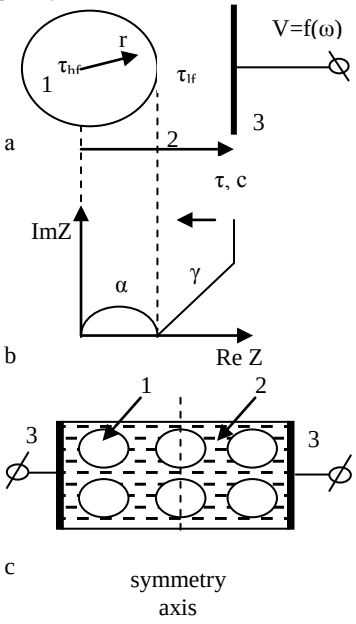

Figure 4. Geometric representation of nanopowder system with respect to the electrical properties (a); the spatial relationship (r) and time (τ) coordinate with the shape of the hodograph (b); model representation in accordance with the actual spatial distribution of the phase (c), where
1 - the volume of the dielectric nanoparticles;
2 - ion-conductive dispersion medium;
3 – electrode;
r - radius vector;
τ - typical response time (time constant) of the structural elements).

Experimental dependence of signal amplitude of spin -eho time is shown in Figure 5, a. It can be approximated by the equation:

$$A(\tau) = a \cdot \exp(-2\tau / T_{2,c}) + b \cdot \exp(-2\tau / T_{2,f}), \quad (1)$$

where 2τ - latency spin echo signal relative to the first RF pulse, a, b - coefficients, $T_{2,c}$, $T_{2,f}$ - characteristic spin-spin relaxation times of hydrogen nuclei ^{1}H.

The presence of two characteristic times of spin-spin relaxation $T_{2,c}$ = 84.4mks and $T_{2,f}$ = 332mks indicates the presence of two states of water with different mobility in a sample. Thus, the results of the spin-echo - studies indicate that the atmosphere surrounding the nanoparticle is composed of two parts.

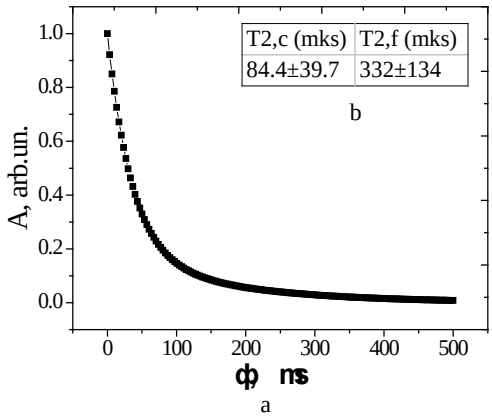

Figure 5. The experimental dependence of the damping of the spin-echo signal (a) and the values of the relaxation times of the magnetic moments of the hydrogen nuclei 1 H (b)

3.4. Schematic structure of adsorption layer on the surface of nanoparticles based on ZrO_2

Modern theory of structure of electrical double layer (EDL) suggests that EDL consist from two parts (Figure 6,a) [27, 28, 29, 30]. One part is located directly at the interface (Helmholtz layer or an adsorption layer), another - in the diffuse part with thickness χ, which depend from the properties of dispersion medium and ions of inner layer. Value of the potential in the Helmholtz layer at a distance from the potential formed ions decreases linearly from φ_o to potential of diffusion layer φ_δ, and then changed exponentially (Figure 6, b).

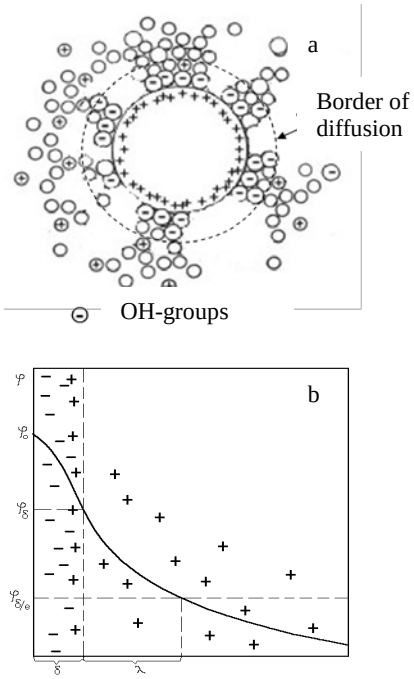

Figure 6. The electric double layer of ZrO_2 particles (a) and change of its potential (b).

Thus, in this case, two states of water molecules, with different degree of mobility, obviously, are related to chemically and physically adsorbed water. Chemically bounded with the surface of nanoparticles molecules of water with relatively low spin-spin relaxation times $T_{2,S}$ are located in the interior part of ion shell of particles - in the adsorption layer, they form a charged potential formed layer. Molecules with long times $T_{2,f}$ match to physically bounded water. They located in the outer space of particle - in diffusion layer. Ions of diffuse layer,

according to the EIS- analysis, provide continuity of electrical properties of nanopowder dispersed system.

Conclusion

Comprehensive investigation of nanopowder system ZrO_2-3mol% Y_2O_3 (700 ° C, 2h) was carried out. Presence of a dispersion medium (ionic atmosphere) in the space between the particles was established. Presence of two forms of the existence of water in the dispersion medium, characterized by the spin-spin relaxation times of hydrogen nuclei 1H., Respectively, T2, c = 84.4mks and $T_{2,\ f}$ = 332mks was observed . Based on modern theory of structure of EDL, it concluded that presented in system forms of water corresponds to molecular and chemically forms of bounded with nanoparticles surface. It was found that dispersion medium has electrical conductivity, which has a diffusion character It value is $1.03 \cdot 10^{-4}$ $(Ohm \cdot m)^{-1}$ and conductivity of the material nanoparticles is $6.5 \cdot 10^{-6}$ $(Om \cdot m)^{-1}$.

Revealed continuity of electrical properties of dispersion medium has practical value. It is confirms the possibility of technical implementation of managed energy exchange between heterophase bonder of dispersed system and external environment.

Acknowledgments

The authors are thankful for the H2020-MSCA-RISE-2015 Programme, the project n691010 HUNTER for financial support of their work.

Work was supported by grant number 16-33-50010 Project RFFI.

References

1 R.A. Andrievsky, A.M. Glaser / Size effects in nanocrystalline materials. Mechanical and physical properties // Physics of Metals and Metallography, 2000, Vol.89, №1, P. 91 – 112.
2 K.I. Yanushkevich, O.F. Demchenko, T.E. Konstantinova, I.A. Danilenko / Magnetism of doped zirconium dioxide nanopowders / FTVD, Vol.13, No 3, P. 48-54, 2003.
3 I.D. Morozov, L.I.Trusov, VN Lapovok / Physical phenomena in ultrafine media // - M .: Energoatomisdat, 1984. - 224p.
4 J. Robert Kelly Stabilized zirconia as a structural ceramic An overview/ J. Robert Kelly, Isabelle Denry // Dental Materials. Vol. 24, Issue 3, 2008, P.289-298.
5 V.Y. Gavrilov / Research of microporous structure of zirconium dioxide //Kinetics and Catalysis, Vol.41, No5, 2000, P.786-790.
6 Yu.Yu.Bacherikov, S.V.Optasyuk, T.E.Konstantinova, I.A.Danilenko / White light of termodoped zirconia // Proceedings of the V International Scientific-Technical Conference "Microelectronic converters and devices on their basis" Mapp, December 5-8, 2005., Baku-Sumgayit, P. 296-299.
7 Despotuli A.L., Nikolaichik V.I. / A step towards nanoionics // Solid State Ionics, Vol.60, 1993, P 275-278.
8 Tsubota S. / High-capacitance capacitors by Murata make smaller power supplies // AEI, Vol. 12, 2005, P. 41-43.
9 B.C Steele, Heinzel, A.. / Materials for fuel-cell technologies" // Nature, Vol. 414 (Nov 15), 2001, P 345–352.
10 S.P. Badwal / Review of Progress in High Temperature Solid Oxide Fuel Cells / Journal of the Australian Ceramics society // Vol.50 No(1), 2005.
11 Y.I. Korolkov, I.D. Kashcheev / High-strength ceramics based on zirconia powder // Glass and ceramics, No 6, 2002, P.11 - 15.
12 Directive 2010/31/EU of the European Parliament and of the Council, http://eur-lex.europa.eu/ LexUriServ/LexUriServ.do?uri=OJ:L:2010:153:0013:0035:EN:PDF
13 N.V. Keltsev / Fundamentals of adsorption technology // M .: Chemistry, 1976., 512 p.
14 N.F. Uvarov / Ionic of nanoheterogeneous materials // Russian Chemical Reviews, Vol.76, No 5, 2007, P.454-473.
15 O.L. Khasanov / Problems of compacting nanopowders and methods of their solutions // Physical chemistry of ultrafine systems. Collection of scientific works of VI All-Russian (International) Conference. 19 -23 August 2002 Tomsk. M .: MIFI, 2003, P.180 - 183.
16 Weertman J.R. et al. / Structure and Mechanical Behavior of Bulk Nanocrystalline Materials // MRS Bulletin, No 2, 1999, P.44-50.
17 A.D. Zimon, E.I. Andrianov / Autohesion of bulk materials // Moscow, 1978.
18 A.L. Despotuli, A.V. Andreeva / High-capacity capacitors for 0.5-volt future nanoelectronics // Modern electronics, No7, 2007, P. 24-29
19 A.S. Doroshkevich, I.A. Danilenko, T.E. Konstantinova, V.A. Glazunova, S.A. Sinyakina / Diagnosis of nanopowder systems based on zirconia by transmission electron microscopy // "Electron microscopy and strength of materials." Vol. 13, 2006, P.151-159.
20 http://www.abc.chemistry.bsu.by/vi/analyser/.
21 E.V. Buyanova, Y. Emelyanov / Impedance spectroscopy of electrolytic materials / // Ural Ekaterinburg .: State university. 2008, 70p.
22 R.D. Apostolova, O.V. Kolomoets, V.P Tysyachnyy, E.M. Shembel / Discharge capacity of lithium battery layout and impedance of electrodes based on electrolytic iron sulfide depending on size of particles // Questions of chemistry and chemical technology, No2, 2009. P. 137 - 143.
23 M.E. Kompan, V.P. Kuznetsov, V.G. Malishkin / Non-linear impedance of solid-state energy storage capacitors, supercapacitors // Technical Physics, Vol. 80, No. 5. 2010, P. 100 - 106.
24 S.V. Gnedenkov, S.L. Sinebryukhov, V.I. Sergienko / Modeling of electrochemical impedance phase boundary of metal oxide heterostructure / electrolyte // Electrochemistry, Vol 42, No 3, 2006, P. 235-250.
25 A.A. Vashman, I. S. Pronin / Nuclear magnetic relaxation spectroscopy // M .: Energoatomizdat, 1986, 232 pp.
26 T. Farrar, E. Becker / Pulsed anf Fourier spectroscopy of NMR // Moscow, 1973, 300p.
27 S.S. Voyutsky / Course of Colloid Chemistry // M .: Chemistry, 1976, 512 p..
28 D.A. Fridrihsberg / Course of Colloid Chemistry // L .: Chemistry, 1995. - 400 p. (1984. - 368 p.)
29 Y.G. Frolov / Course of Colloid Chemistry // M .: Chemistry, 1988. - 464 p. (1982 - 400)p.
30 E.D. Shchukin, A.V. Pertsov, E.A. Amelina / Colloidal chemistry // M .: Izd. University Press, 2004. - 445 p. (1982. - 348 pp.)