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Physical and Chemical Properties of Semiconductor Adsorbents of InP–CdB^{VI} Systems

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Abstract—Comparative results of the synthesis, X-ray, Raman spectroscopy, and electron-microscopy studies, and determination of the acidity of the surface of solid solutions (pH_{iso}) of InP–CdS, InP–CdTe systems, differing in the second binary components (CdS, CdTe) and nevertheless including the common element (Cd) are presented. The formation of substitutional solid solutions with a cubic sphalerite structure in both systems is demonstrated. Their surfaces are of a slightly acidic nature at a greater degree of acidity of the solid-solution surfaces of the InP–CdTe system. With a variation in the system composition, the studied properties change both steadily (lattice parameters, interplanar distances) and drastically (theoretically calculated crystal density, average number of particles, pH_{iso}). At the same time, the system generality is found in correlations between the $pH_{iso} = f(x_{CdS})$, $\rho_r = f(x_{CdS})$ and $pH_{iso} = f(x_{CdTe})$, $\rho_r = f(x_{CdTe})$ dependences. The noted generality and difference in the systems are explained by the predominant, but different influence on the solid-solution properties of the second binary components (CdS, CdTe) and the "behavior" of the common element (Cd). Based on the correlations between the plotted diagrams "property–composition", the possibility of the easier search for advanced materials suitable for the fabrication of sensors is proposed.

Keywords: adsorbents–solid solutions, physical and chemical properties, regularities, correlations, new materials for sensors

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INTRODUCTION

The objects of research in this work were multicomponent diamond-like semiconductor solid solutions of the InP–CdS and InP–CdTe systems. In systems such as those belonging to a new type of heterovalent substitution, both cation and anion formers with different valences are in different groups of the periodic system. Accordingly, in contrast to isovalent solid solutions, in them the atoms-substituents in the lattice of the main substance behave like electrically active impurities, which leads to doping of the main substance, a possible change in the crystal lattice and, as a result, to a change in the physical and physical-chemical properties of the solid solutions. Therefore, with a change in their composition, it is logical to expect a manifestation of both a statistical and an extreme factor in the changes in the properties. The latter is especially interesting from the point of view of the search for new promising materials for modern technology, including nano-, sensor technology, and heterogeneous catalysis.

For a predictable choice of such systems, it is useful to compare them, which is provided in this work. Upon preliminary, external examination, the selected systems differ in terms of the second binary components (CdS, CdTe) and at the same time include a common element (Cd).

EXPERIMENTAL

For preparation of the solid solutions $(InP)_x(CdS)_{1-x}$ ($x = 0.93, 0.95, 0.97$), $(InP)_x(CdTe)_{1-x}$ ($x = 0.09, 0.12, 0.16, 0.18$), we used the method of isothermal diffusion of the initial binary compounds (InP and CdS, InP and CdTe), updated taking into account their physical and physical-chemical properties, in preliminarily justified modes, according to special temperature heating programs [1, 2]. Intensification of the synthesis of the solid solutions was facilitated by mechanical activation at its initial stage. The solid solutions were certified by the results of X-ray, electron microscopy and Raman spectroscopy studies.

For the studies, solid solutions and binary components were used in the form of finely dispersed powders ($S_{sp} = 0.34–1.2$ m^2/d) and thin films ($d = 20–100$ nm). The films were prepared by discrete thermal sputtering in vacuum onto the electrode pads of piezoelectric quartz resonators [3, 4].

X-ray studies were carried out on BRUKER AXS Advance D8 Power X-ray devices (CuK_α radiation,

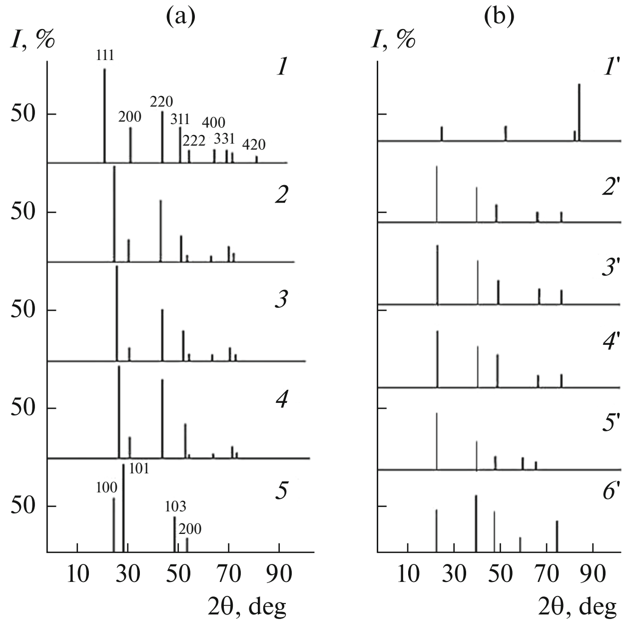

Fig. 1. Linear X-ray diffraction patterns of components of the InP–CdS (a) and InP–CdTe (b) systems: (*1*, *1'*) InP; (*2*) $(InP)_{0.97}(CdS)_{0.03}$; (*3*) $(InP)_{0.95}(CdS)_{0.05}$; (*4*) $(InP)_{0.93}(CdS)_{0.07}$; (*5*) (CdS); (*2'*) $(InP)_{0.18}(CdTe)_{0.82}$; (*3'*) $(InP)_{0.16}(CdTe)_{0.84}$; (*4'*) $(InP)_{0.12}(CdTe)_{0.88}$; (*5'*) $(InP)_{0.09}(CdTe)_{0.91}$; (*6'*) CdTe.

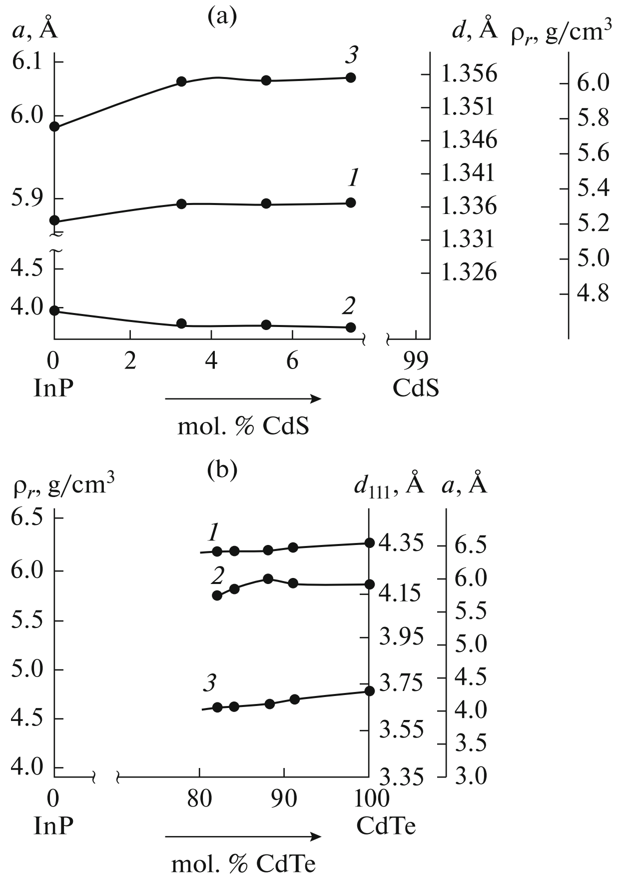

Fig. 2. Dependences on the compositions of the parameter values (*a*) (*1*) interplanar distances (d_{331}, d_{111}) (*3*) crystal lattices and (*2*) X-ray density (ρ_r) for the components of the InP–CdS (a) and InP–CdTe (b) systems.

$\lambda = 0.154056$ nm, $T = 293$ K) using a Lynxeye position-sensitive detector and DRON-3 ($CuK_{\alpha\beta}$ radiation, $\lambda = 0.154178$ and 0.139217 nm, $T = 293$ K) according to the method of surveying in the far-corner region [5–7]. Electron microscopic studies were performed on a JCM-5700 scanning electron microscope equipped with a JED 2300 attachment for energy dispersive analysis [8]. The Raman spectra were recorded on an RFS-100 Fourier spectrometer with a resolution of 1 cm^{-1} [9].

The surface (acid-base) properties were judged from the values of the pH index of the isoelectric state (pH_{iso}), which were determined by the method of hydrolytic adsorption [10]. At the same time, we found the pH of the medium in which the ampholyte adsorbent removes equal (insignificant) amounts of H^+ and OH^-. The role of ampholyte adsorbents was played by the semiconductor components of the InP–CdS, InP–CdTe systems with characteristic isoelectric points corresponding to the minimum solubility.

The reproducibility and accuracy of the experimental data were checked by the results of parallel measurements using methods of mathematical statistics and processing of the results of quantitative analysis. Statistical processing of the obtained values, calculation of the measurement errors, and the construction and processing of dependence diagrams were performed using the Stat-2, Microsoft Excel, and Origin computer programs.

DISCUSSION

The results of X-ray studies (Figs. 1, 2) made it possible to prove the formation of substitutional solid solutions in InP–CdS and InP–CdTe systems (at given compositions), to determine their structure, and to establish the prevalence of the statistical factor during their formation with some extreme contribution. Let us consider the X-ray diffraction patterns (Fig. 1). We note: the lines corresponding to the resulting substitutional solid solutions are shifted relative to the lines of the initial binary compounds (InP and CdS, InP and CdTe) at their constant number; and there are no additional lines corresponding to unreacted binary compounds, blurring of the main lines (which indicates completion of the synthesis process and, additionally, the formation of solid solutions). The position and intensity distribution of the main lines indicate the cubic structure of sphalerite in

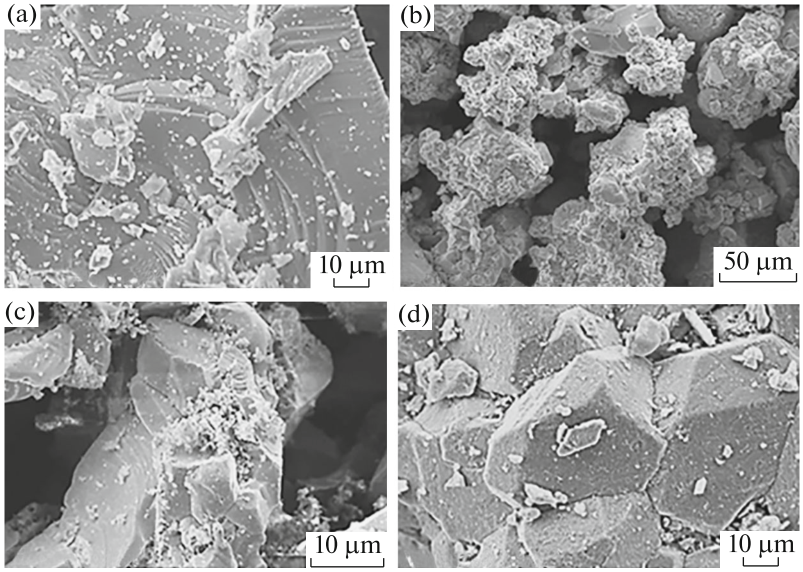

Fig. 3. SEM images of the InP powders (a), $(InP)_{0.18}(CdTe)_{0.85}$ (b), $(InP)_{0.09}(CdTe)_{0.91}$ (c), CdTe (d).

all components of the systems (InP, CdS, CdTe, $(InP)_x(CdS)_{1-x}$, $(InP)_x(CdTe)_{1-x}$).

The formation of substitutional solid solutions in the systems under study unambiguously proves a smooth, close to linear dependence on compositions calculated on the basis of X-ray diffraction patterns of the parameter values (a) and interplanar distances (d_{hkl}) of the crystal lattices (Fig. 2). Deviations from Vegard's rule of dependences $\rho_r = f(x_{CdS})$, $\rho_r = f(x_{CdTe})$ (Fig. 2) can be explained by the influence of the uneven distribution of cation–anion complexes caused by complex internal processes accompanying the formation of the solid solutions [11]. This is also consistent with the results of electron-microscopic studies, which demonstrated the polycrystalline structure of the components of the systems with an inhomogeneous distribution of crystallites (Fig. 3).

We have repeatedly noted the admissibility of deviations from the linear dependences of the bulk characteristics of semiconductor solid solutions on the basis of the detailed analysis of studies on these (for example, [1, 12–14]). Of particular interest in this respect is work [15], whose authors associate deviations from the linear dependence $\alpha = f(c)$ with the possible loss of a certain amount of cadmium during the synthesis of solid solutions of the InSb–CdTe system, which, in comparison with other elements of the system (In, Sb, Te), has the lowest boiling point and the highest vapor pressure.

The Raman spectra (Raman spectra) supplemented the above facts. They confirmed the formation of substitutional solid solutions: in the ranges of characteristic frequencies, there are no peaks typical for the binary component InP (Fig. 4).

On the basis of electron-microscopic studies, the elemental composition, and the average sizes (d_{av}) and average numbers (n_{av}) of predominant particles of solid solutions and binary components of the systems were also determined. The elemental compositions practically coincide with the specified molar compositions; the average numbers of predominant particles are consistent with their average sizes (Table 1). At the same time, of note are the correlations between the density values (ρ_r) found from X-ray diffraction patterns and the average number of particles found from SEM images. Given the impact n_{av} on the coordination unsaturation of surface atoms responsible for Lewis acid sites, we can talk about a possible rough estimate by n_{av} of the suitability of the materials obtained for the manufacture of sensors for trace gases of a certain electronic nature.

Interestingly, this prediction is confirmed by the results of direct studies of the surface properties of system components. On the basis of studies of the surface (acid-base) properties, the values of the average strength of acid sites, i.e., the pH of the isoelectric state of the original (exposed to air) surfaces, were determined. They amount to 6.2–6.6 and 5.3–6.3 for components of the InP–CdS and InP–CdTe systems, respectively, indicating the weakly acidic nature of the surfaces and their expected increased activity with respect to the main gases [1, 4]. Indeed, under the influence of the main gas, ammonia, the acidity of the surfaces decreases (pH_{iso} increases, within 0.9) in contrast to the effects of acid gas, NO_2 (pH_{iso} decreases, within 0.6).

Upon a change in the compositions of the systems, the pH_{iso} changes drastically (Fig. 5), which testifies to competition in the manifestations of Lewis and Bron-

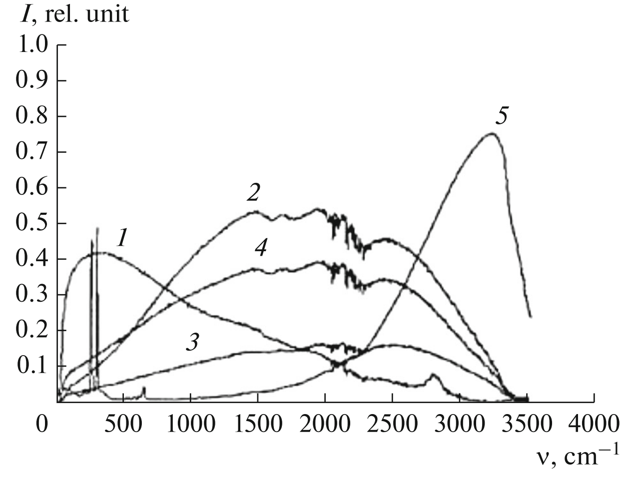

Fig. 4. Raman spectra in the region of anti-Stokes radiation of the components of the InP–CdS system: (*1*) CdS; (*2*) $(InP)_{0.93}(CdS)_{0.07}$; (*3*) $(InP)_{0.95}(CdS)_{0.05}$; (*4*) $(InP)_{0.97}(CdS)_{0.03}$; (*5*) InP.

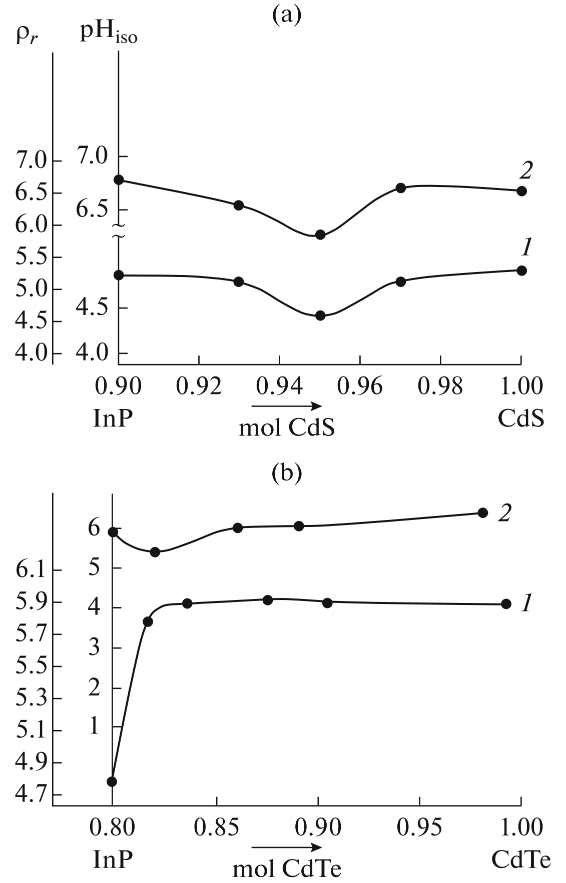

Fig. 5. Dependences of the X-ray density ρ_r on the compositions of components of the InP–CdS (a) and InP–CdTe (b) systems (*1*) and pH of the isoelectric state of surfaces pH_{iso} (*2*).

sted centers, all the more so possible in the case of the already noted complex internal processes accompanying the formation of solid solutions [1, 4]. Undoubtedly, the revealed correlations between the bulk and between the bulk and surface properties of components of the InP–CdS, InP–CdTe systems are of scientific and practical interest. Thus, on the one hand, the maximum of the average number of particles dominant in the components (n_{av}) corresponds to the maximum of the X-ray density (ρ_r); a decrease in n_{av} corresponds to a decrease in ρ_r (Fig. 6). On the other hand, the minimum pH_{iso} corresponds to either the minimum of the X-ray density or its sharp decrease at a given composition (Fig. 5). With this correlation between pH_{iso} and ρ_r the decisive role of the Lewis centers is clearly traced, for which surface atoms, coordination unsaturation, and, accordingly, the activity of which increases with decreasing density are mainly responsible. And since there is, in turn, a direct connection between ρ_r and n_{av}, the above forecast about the possible preliminary assessment of the surface activity by n_{av} is logically confirmed.

A correlation between the bulk and surface properties and the effect of the bulk properties on the surface properties were found not only within individual studied systems, but also when comparing them. We note the following: the surfaces of solid solutions of the InP–CdTe system turned out to be relatively more acidic (pH_{iso} are 5.3–6.0), compared with the surfaces of solid solutions of the InP–CdS system (pH_{iso} are 6.2–6.6). Here, the predominant and dissimilar effect on the properties of solid solutions of systems of second binary components (CdS and CdTe) is affected: the presence of cadmium sulfide in the InP–CdS system, which differs from the second component of the InP–CdTe system, cadmium telluride, by a larger electronegativity difference ($\Delta x_{CdS} = 0.88$; $\Delta x_{CdTe} = 0.49$) and, accordingly, a larger fraction of the ionic bond, determined a more basic character, i.e., elevated pH_{iso} values of the solid-solution surfaces $(InP)_x(CdS)_{1-x}$.

In accordance with what has already been said, the commonality between the systems, manifested in a correlation between the extreme dependences of

Table 1. Molar composition and the corresponding elemental composition of components of the InP–CdTe system

Molar composition	Elemental composition
InP	$In_{0.51}P_{0.49}$
$(InP)_{0.18}(CdTe)_{0.82}$	$In_{0.10}P_{0.08}Cd_{0.43}Te_{0.39}$
$(InP)_{0.16}(CdTe)_{0.84}$	$In_{0.08}P_{0.08}Cd_{0.42}Te_{0.42}$
$(InP)_{0.12}(CdTe)_{0.88}$	$In_{0.07}P_{0.05}Cd_{0.45}Te_{0.43}$
$(InP)_{0.09}(CdTe)_{0.91}$	$In_{0.05}P_{0.04}Cd_{0.51}Te_{0.40}$
CdTe	$Cd_{0.495}Te_{0.505}$

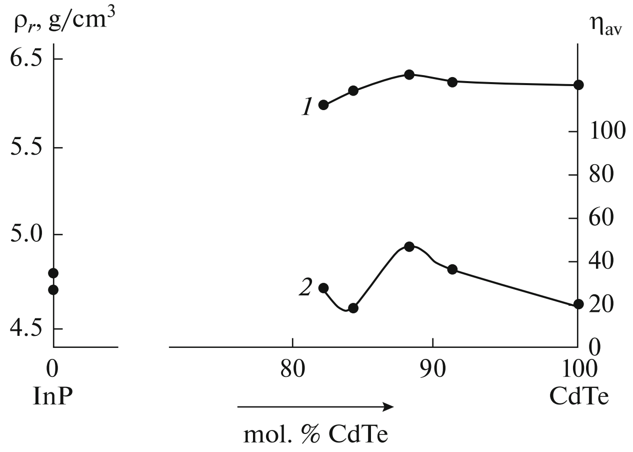

Fig. 6. Dependences of the X-ray density ρ_r on the composition of the components of the InP–CdTe system (*1*) and the average number of dominant particles n_{av} (*2*) in the range of their sizes 4–6 μm.

$pH_{iso} = f(x_{CdS})$, $\rho_r = f(x_{CdS})$ and $pH_{iso} = f(x_{CdTe})$, $\rho_r = f(x_{CdTe})$ (Fig. 5), can to a certain extent be related (with obligatory consideration of the complexity of internal processes accompanying the formation of solid solutions) to a certain loss in the synthesis of solid solutions of a common element, i.e., cadmium, which, in comparison with other elements (In, P, Te), has the lowest boiling point and the highest vapor pressure [15].

CONCLUSIONS

Using the method of isothermal diffusion of the initial binary compounds (InP and CdS, InP and CdTe), updated taking into account their physical and physical-chemical properties, solid solutions of the InP–CdS, InP–CdTe systems were obtained. X-ray, electron microscopic, and Raman spectroscopic studies have been carried out, which made it possible to supplement information on the properties of multicomponent diamond-like semiconductors and to certify the obtained solid solutions as substitutional solid solutions with a cubic sphalerite structure.

The surface (acid-base) properties of the solid solutions and binary components of the InP–CdS, InP–CdTe systems have been studied. The weakly acidic nature of the surfaces of the components of both systems (binary and solid solutions) is shown at an increased acidity of the surfaces of solid solutions of the InP–CdTe system. The regularities of changes with the composition of the studied bulk and surface properties, which are both steady and drastic, have been established. The correlations between them and the corresponding property–composition state diagrams are revealed.

The found commonality and differences in the properties of solid solutions of the systems are explained by the dominant (but dissimilar) influence on them of the second binary components (CdS, CdTe) and the "behavior" of the common element (Cd). Based on the correlations between the plotted property–composition state diagrams, the possibility of the easier search for new materials for the manufacture of corresponding sensors is shown.

REFERENCES

1. I. A. Kirovskaya, *Solid Solutions of Binary and Multicomponent Semiconductor Systems* (Omsk. Gos. Tech.Univ., Omsk, 2010) [in Russian].
2. I. A. Kirovskaya, E. V. Mironova, O. V. Ushakov, A. A. Deeva, and A. V. Yurieva, Proc. Eng. **152**, 681 (2016). https://doi.org/10.1016/j.proeng.2016.07.673
3. V. A. Kas'yan, *Indium Antimonide Thin Films: Preparation, Properties, Application* (Shtiintsa, Kishenev, 1989) [in Russian].
4. I. A. Kirovskaya, *Physicochemical Properties of Binary and Multicomponent Diamond-Like Semiconductors* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2015) [in Russian].
5. S. E. Mirkin, *Handbook of X-Ray Structural Analysis* (Fizmatlit, Moscow, 1961) [in Russian].
6. S. S. Gorelik, L. N. Rastorguev, and Yu. A. Skakov, *X-Ray and Electro-Optical Analysis* (Metallurgiya, Moscow, 1970) [in Russian].
7. E. F. Smyslov, Zavod. Lab., Diagn. Mater. **72** (5), 33 (2006).
8. J. I. Goldstein, D. E. Newbury, P. Echlin, et al., *Scanning Electron Microscopy and X-Ray Microanalysis* (Plenum, New York, 1981).
9. M. M. Sushchinskii, *Raman Scattering of Light: Structure of Matter* (Nauka, Moscow, 1981) [in Russian].
10. L. G. Maidanovskaya, *Catalytic Reactions in Liquid Medium* (Akad. Nauk KazSSR, Alma-Ata, 1963), p. 212.
11. A. R. West, *Solid State Chemistry and Its Applications* (Wiley, Chichester, 1984), Part I.
12. I. A. Kirovskaya, *Surface Properties of Diamond-Like Semiconductors: Solid Solutions* (Irkutsk. Gos. Univ., Irkutsk, 1988) [in Russian].
13. I. A. Kirovskaya, Zh. Fiz. Khim. **59**, 194 (1985).
14. I. A. Kirovskaya, P. E. Nor, E. V. Mironova, and T. A. Kirovskaya, *Adsorbents Based on* $A^{II}B^{VI}$–$A^{II}B^{VI}$ *Systems: Materials for Semiconductor Gas Analysis* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2018) [in Russian].
15. V. A. Brodovoi, N. G. Vyalyi, and L. M. Knorozok, Neorg. Mater. **33**, 303 (1997).