Volume and surface properties of solid solutions of systems A\textsuperscript{III}B\textsuperscript{V}-CdS, A\textsuperscript{II}B\textsuperscript{VI}-CdS

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Abstract. Bulk (crystal-chemical, structural) and surface (chemical composition of the surface, acid-base) properties of solid solutions of the InSb-CdS, CdTe-CdS systems (compared to the initial binary compounds InSb, CdTe, CdS), prepared in the form of fine powders and thin films have been studied in an integrated manner involving up-to-date techniques. Solid solutions are certified as substitution solid solutions with a wurtzite structure.

The consistent patterns have been revealed in the studied properties changes with changes in the systems compositions that have both smooth (subject to Vegard's law) and extreme nature. The predominant influence on them by the first binary components (InSb, CdTe) has been demonstrated and justified.

The acidic sites' nature, strength, concentration have been determined. An increased sensitivity of the system components surfaces (at pH\textsubscript{iso}\textless 7) to the main gases has been found. The most active of them have been recommended as primary sensors materials for measuring cells for ammonia micro impurities.

Keywords - solid solutions, bulk and surface properties, consistent patterns, selective sensitivity, measuring cells.

1. Introduction

Scientific and technological progress in areas such as nanotechnology, semiconductor gas analysis, heterogeneous catalysis requires systematic search for new materials and methodical knowledge of their bulk and surface properties. Multicomponent diamond-like semiconductors - solid solutions based on compounds of the A\textsuperscript{III}B\textsuperscript{V}, A\textsuperscript{II}B\textsuperscript{VI} type seem to be promising, smoothly and (or) extremely changing the properties depending on the composition and keeping unrevealed secrets in their “behavior” due to the complex internal processes accompanying their formation.

Such multicomponent semiconductors – objects of research in the present work include solid solutions of the InSb-CdS, CdTe-CdS systems, distinguished by the first initial binary compounds of the (A\textsuperscript{III}B\textsuperscript{V}, A\textsuperscript{II}B\textsuperscript{VI}) type and (InSb, CdTe) composition. The effect of these compounds on the solid solutions properties within each system as well as their distinguished effects upon contact with the same second compound (CdS) is advantageous.

2. Problem statement

To study the bulk (crystallochemical, structural) and surface (chemical composition of the surface, acid-base) properties of solid solutions of the InSb-CdS, CdTe-CdS systems, compared to each other and to the initial binary compounds (InSb, CdTe, CdS). To reveal consistent patterns in the studied properties changes with changes in the systems composition. To define the relative contribution of the initial binary compounds to the solid solutions “behavior”. To assess the selective sensitivity of the
systems components surfaces with respect to gases of different electronic nature. To identify the most active components – promising materials for measuring cells manufacture.

3. Theory

Encouraging outlook to obtain advanced materials for modern technology, including nano-, sensor technology, semiconductor gas analysis is undoubtedly found in a family of diamond-like semiconductors, interest in which, starting with elementary, then binary semiconductors, has been constantly increasing. A separate place in this family is to be occupied by multicomponent semiconductors - solid solutions based on binary semiconductors, primarily of the A<sup>III</sup>B<sup>V</sup>, A<sup>II</sup>B<sup>VI</sup> type as they involve more extensive search possibilities. The latter are defined by unique properties of the initial binary compounds (electrophysical, photo- and isoelectric, optical) as well as by possibilities not only to regulate properties by changing the composition, but also to reveal particularly interesting unexpected (extreme) effects. For more efficient use of these possibilities, formation of a less time-consuming search it is necessary to expand the range of complex systems under study along with comprehensive study of bulk and surface properties (when complex systems are compared with each other and with their original binary compounds), establishment of interconnected patterns, implementable forecasts.

It is the central area of focus of the present work as an integral part of long-term research performed by the team represented by the authors.

4. Experimental part

Solid solutions (InSb)<sub>x</sub>(CdS)<sub>1-x</sub> (x = 20, 40, 65, 95 mol. %), (CdTe)<sub>x</sub>(CdS)<sub>1-x</sub> (x = 39, 50, 76, 84 mol. %) in the form of powders (S<sub>sp</sub> = 0.3 – 0.91 m<sup>2</sup>/g) and films (d = 20-100 nm) were obtained respectively by method of binary compounds (InSb and CdS, CdTe and CdS) isothermal diffusion, improved with regard to for specific systems in vacuumed, sealed quartz ampoules at temperatures above the melting point of the low-melting compound (InSb) and below the melting point of the high melting compounds (CdTe, CdS), according to the created program [1] and discrete thermal spraying in vacuum (T<sub>cond</sub> = 298 K, P = 1.33·10<sup>-3</sup>) onto the piezoquartz resonators electrode sites, followed by homogenizing annealing [2, 3].

The solid solutions obtaining and their structure were judged mainly by the results of X-ray studies involving the results of thermographic, submicroscopical, and IR spectrometric studies. X-ray studies were carried out on the DRON-3 diffractometers (CuK<sub>a</sub> - radiation, λ = 0.154178 and 0.1339217 nm) and Advance D8 Powder X-ray Diffractometer by BRUKER AXS (CuK<sub>a</sub> radiation, λ = 0.1540 nm, T = 293 K) involving wide-angle survey technique [4, 5]; thermographic (differential thermal and gravimetric analysis) - on the differential thermal analyzer DTG-60, Shimadzu within the temperature range 303 - 1273 K [1, 6].

Submicroscopical studies were performed with a scanning electron microscope JSM-5700, equipped with a nitrogen-free x-ray energy-dispersive spectrometer JED-2300 [7]; IR spectroscopic studies were conducted on the Fourier spectrometer infrared Infra-LUM FT-02 with a repeated frustrated internal reflectance attachment (crystal material-germanium, spectral range 400-4000 cm<sup>-1</sup>) and Shimadzu spectrometer with a Fourier transformer [1].

Surface (chemical composition of the surface, acid-base properties) of the components of the InSb-CdS and CdTe-CdS systems was studied by IR spectroscopy of a repeated frustrated internal reflectance [1], hydrolytic adsorption (determination of the pH isoelectric state – pH<sub>iso</sub>) [8], mechanochemistry [3], non-aqueous conductometric titration [9].

5. Results and discussion
The positions on the X-ray patterns of the lines of the initial binary compounds (InSb and CdS; CdTe and CdS) mutual diffusion products relative to the lines of the latter, and the lines distribution by intensity (Fig.1) allow saying of substitution solid solutions formation in the InSb-CdS, CdTe-CdS systems with wurtzite structure. An unrestricted mutual solubility of the binary components of the CdTe-CdS system with given compositions and the very limited mutual solubility of the binary components of the InSb-CdS system come under notice: the CdS in InSb solubility interval is 0 - (3-4) mol. %.

As for the concentration dependences of the crystal-chemical and structural characteristics calculated on the basis of the X-ray images (parameters-\(a, c\), crystal lattices interplanar distances- \(d_{hkl}\), density- \(\rho_r\)), they have both a smooth (close to linear) nature (especially within the same structure) and an extreme nature, deviating from Vegard's law (Fig. 2).

Possibility of such deviations with the complexity of the internal processes accompanying the solid solutions formation, has been noted repeatedly (see, for example, [1]).

![Figure 1](image-url)  
**Figure 1.** 1 Line X-ray pattern of the system InSb-CdS components: 1 – InSb; 2 – (InSb)\(_{0.95}\)(CdS)\(_{0.05}\); 3 – (InSb)\(_{0.65}\)(CdS)\(_{0.35}\); 4 – (InSb)\(_{0.40}\)(CdS)\(_{0.60}\); 5 – (InSb)\(_{0.20}\)(CdS)\(_{0.80}\); 6 – CdS

In particular, based on an analysis of the properties and interactions of the elemental constituents of the system’s components, an explanation is meant to be the nonuniform distribution of cationic-anionic complexes [10]. To the above, it is appropriate to note that according to the submicroscopical studies results (Fig. 3), the films of the system’s components are polycrystalline, with an inhomogeneous crystallites distribution, associated in agglomerates with a combination of various sizes grains.

The thermograms of systems’ components (see, for example, Fig. 4) demonstrate endo- and exo-effects, accompanied by an increase in mass in the investigated temperature range and differing in
intensity. Endothermic effects correspond to the melting temperatures of systems’ components, exothermic effects are most likely due to the oxidation products formation since at these temperatures a significant increase in mass occurs.

When analyzing IR spectra of repeated frustrated internal reflectance (Fig. 5) taken mainly to determine the chemical composition of the system components surfaces, a certain regularity in the location of the main absorption bands attracts attention. Namely, with a change in the systems’ compositions, a shift in the peaks corresponding to the valence vibration of molecularly adsorbed \( CO_2 \) (bands 2310, 2340, 2320, 2360 cm\(^{-1}\)) and water (bands 1600, 3650, 1650, 3660, 1660, 3660, 1650, 3680) [1, 11 ± 13] of solid solutions with respect to the same peaks on binary components (Fig. 5).

The concentration dependence of the most displayed particles average number values (\( n_{av} \)) in the components of systems calculated according to the results of submicroscopical studies (according to SEM images) (Fig. 3), correlate in opposite way with the concentration dependence of the theoretical calculated crystal density (\( \rho_r \)): they contain opposite extreme value of the same compositions (Fig.6).

When analyzing the bulk properties dependence (crystal-chemical, structural) of the InSb-CdS, CdTe-CdS systems components on the composition and the corresponding “property-composition” diagrams (Fig. 2), attention is drawn to the determining effect on them not by common binary component (CdS) but the first binary components (InSb, CdTe), which differ from CdS prominently in their properties. For example, the melting point (\( T_{ml} \)), electronegativity difference (\( \Delta x \)), forbidden bandwidth (\( \Delta E \)) are [11]:

- for InSb, CdS 525 and 1750 °C; 0.1 and 0.8; 0.18 and 2.42 eV;
- for CdTe, CdS 1092, and 1750 °C; 0.4 and 0.8; 1.51 and 2.42 eV.

Figure 2. Dependence on the parameter values composition of crystal lattices (\( a, c \)), interplanar distances (\( d_{hkl} \)) and theoretical calculated crystal density (\( \rho_r \)) of the system InSb-CdS (I); CdTe-CdS (II) components; W – wurtzite, S – sphalerite.
Figure 3. SEM - images of powders CdTe (a), solid solution (CdTe)\textsubscript{0.5}(CdS)\textsubscript{0.5} (b) and CdS (c) in phase contrast mode

Figure 4. DTA (a) and DTGA curves (b): 1 – InSb; 2 – (InSb)\textsubscript{0.99}(CdS)\textsubscript{0.01}; 3 – (InSb)\textsubscript{0.98}(CdS)\textsubscript{0.02}; 4 – (InSb)\textsubscript{0.97}(CdS)\textsubscript{0.03}

That explains the differences in the nature of the indicated dependences within the framework of the InSb-CdS, CdTe-CdS systems (Fig. 2).

According to IR spectra (Figure 5), the chemical composition of the surfaces of binary compounds (InSb, CdTe, CdS) and air-exposed solid solutions (InSb)\textsubscript{x}(CdS)\textsubscript{1-x}, (CdTe)\textsubscript{x}(CdS)\textsubscript{1-x} is represented mainly by adsorbed water molecules, OH\textsuperscript{-} groups (1650, 3650-3680 cm\textsuperscript{-1}bands), carbon-containing compounds (1100 cm\textsuperscript{-1} (CO), 2340-2350 cm\textsuperscript{-1} (CO\textsubscript{2}), 2950 - 2970, 980 cm\textsuperscript{-1} (С-Н)) and surface atoms’ products of oxidation [1, 11 – 13].

After thermal vacuum treatment (up to 10\textsuperscript{-4} Pa), the surfaces are virtually completely free from adsorbed impurities and, in a large measure, from oxides [3, 12].

Based on the results of integrated research of the acid-base properties of the InSb-CdS and CdTe-CdS systems components surfaces, the force, nature, concentration of acid sites, selectivity of surfaces with respect to gases of different electronic nature were determined.

According to the acid sites strength (the surface isoelectric state pH values – $\text{pH}_\text{iso}$), the components of the systems are arranged in series:

\[
\begin{align*}
(\text{InSb})\textsubscript{0.98}(\text{CdS})\textsubscript{0.02} & > (\text{InSb})\textsubscript{0.99}(\text{CdS})\textsubscript{0.01} > \text{CdS} > \text{InSb} > (\text{InSb})\textsubscript{0.97}(\text{CdS})\textsubscript{0.03}, \\
\text{CdS} & > (\text{CdTe})\textsubscript{0.39}(\text{CdS})\textsubscript{0.61} > (\text{CdTe})\textsubscript{0.5}(\text{CdS})\textsubscript{0.5} > (\text{CdTe})\textsubscript{0.76}(\text{CdS})\textsubscript{0.24} > (\text{CdTe})\textsubscript{0.84}(\text{CdS})\textsubscript{0.16} > \text{CdTe}.
\end{align*}
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In such a case, the $\text{pH}_\text{iso}$ values stay within the limits of faintly-acid areas (5.98 – 6.94 and 5.9 – 6.5, respectively), varying with the composition of the systems extremely in the first case and smoothly in the second (Fig. 7). Nevertheless, in the first and second cases, the influence of the second, common binary component – CdS, varying in forbidden bandwidth ($\Delta E$), greater difference in electronegativities and in a logical way - by larger proportion of the ionic link is noticeable.
**Figure 5.** IR spectra of repeated frustrated internal reflectance of the system CdTe-CdS components (а): CdTe (1); (CdTe)$_{0.84}$(CdS)$_{0.16}$ (2); (CdTe)$_{0.76}$(CdS)$_{0.24}$ (3); (CdTe)$_{0.4}$(CdS)$_{0.6}$ (4); (CdTe)$_{0.5}$(CdS)$_{0.5}$ (5); CdS(6) air-exposed and CdS (6), vacuum treated at 338 К during 2 h (1) and after ammonia adsorption at 338 К and $P_a = 15$ Pa (2).

**Figure 6.** Dependence on composition of the average number of the most displayed particles – $n_{av}$ (1) and theoretical calculated crystal density – $\rho_r$ (2) of the system CdS-CdTe components.

**Figure 7.** Differential curves of non-aqueous conductometric titration InSb (1), (CdS) (5) and solid solutions (InSb)$_{0.99}$(CdS)$_{0.01}$ (2), (InSb)$_{0.98}$(CdS)$_{0.02}$ (3), (InSb)$_{0.97}$(CdS)$_{0.03}$ (4).

Like on other diamond-like semiconductors [1, 11, 12], coordinately - unsaturated atoms (Lewis centers) are responsible for the acid sites, the functional ability of which essentially depends on their effective charge, the nearest coordination environment (adjacent OH groups, oxide phase, defects,
principally, vacancy ones), adsorbed molecules of CO₂, H₂O, hydroxyl groups (Bronsted centers). The availability of such is confirmed by IR spectra, containing bands of links formed with them (Fig. 5), the results of mechanochemical studies, non-aqueous conductometric titration (Fig. 7).

According to the results of mechanochemical studies characterizing pH medium changes depending on the time of dispersion in water of coarse powders of the InSb-CdS, CdTe-CdS systems components, air-exposed (in combination with IR spectra), for various compositions, and also for certain time intervals (with the same composition), acidifying (pH decrease) and alkalizing (pH increase) of the medium are noted. Medium acidifying is caused by the water adsorption in the system “dispersed semiconductor-water” with the formation of H₃SbO₄, H₂TeO₄, H₂SO₄, H₂SO₃ acids on the surface (involving B⁵⁺, B⁶⁺ – Sb, Te, S atoms), which under mechanochemical influence transforms into volume [3,12]. Medium alkalizing can be explained by the hydrolysis of weak acids acid residues (H₃SbO₄, H₂TeO₄, H₂SO₃) – SbO₄⁻³, TeO₄⁻², SO₃²⁻.

The results of non-aqueous conductometric titration essentially supplemented the results described above. On that basis, the nature was confirmed, the concentration of acid sites (Сₜₒₑₜ) on the surfaces of the system components was determined, and the change in Cₜₒₑₜ under the influence of gases was evaluated.

The presence of the curves ∆σ/∆V – V (Fig.7) three (for the CdTe-CdS system) and four (for the InSb-CdS system) implies the existence of different types of acid sites on the surfaces and confirms the formation of cationic-anionic complexes distributed unevenly [10].

Following on from the results of multi-year research (see, for example, [1, 3, 11, 12]), it is possible to consider the Lewis acid sites responsible for the first peak and Bronsted acid sites for the rest ones. The results of pHiso measurement confirm this conclusion: with increasing in the systems proportion of the latter, the common binary component (x_CdS), pHiso is shifted to the alkaline area (Fig. 8).

![Figure 8. Dependence on pHiso composition of (a) system InSb-CdS components, air-exposed (1) and system CdTe-CdS components, air-exposed (2) and in ammonia (3); total concentration of acid sites – Cₜₒₑₜ (b) of the system InSb-CdS (1), CdTe-CdS components (2), air-exposed](image)

Calculated for all the peaks of the curves ∆σ/∆V – V, the values of the total concentration of acid sites (Cₜₒₑₜ) with the change of the systems compositions change extremely (Fig. 8), predicting the smallest or greatest activity of their components surfaces towards gases of different electronic nature.

If the surfaces of the InSb-CdS and CdTe-CdS systems components are weakly acidic, their increased, selective sensitivity with respect to the main gases should be expected. The confirmation appears to be the observed changes in the pHiso and IR spectra of the surfaces under the influence of ammonia (Fig. 5, 8). Surfaces acidifying (pHiso increase) (Fig. 8) and the presence of
IR bands are noticed corresponding to adsorption bonds formed as a result of NH$_3$ molecules interaction with acid centers (Fig. 5, [12]).

The point to be emphasized is that in the course of the surface properties study of the InSb-CdS, CdTe-CdS system components, along with the definite influence of the second, common binary component (CdS), the influence of the first binary components (InSb, CdTe) come under notice. As a consequence, we observe more complicated nature of the pH$_{iso} = f (x_{CdS}); C_{tot} = f (x_{CdS}); \Delta \sigma/\Delta V – V$ (Fig.7, 8) for the InSb-CdS system.

6. Conclusions
Solid solutions of InSb-CdS, CdTe-CdS systems, certified as substitution solid solutions with a wurtzite hexagonal structure have been obtained. Their bulk (crystal-chemical, structural) and surface (chemical composition of surfaces, acid-base) properties have been studied when compared to solid solutions with each other and with initial binary compounds (InSb, CdS and CdTe, CdS).

The consistent patterns in the studied properties changes have been established, depending on the compositions of the systems. They possess both smooth (subject to Vegard's law), and extreme nature. The predominant influence on the consistent patterns by the first binary components of the (InSb, CdS) systems has been displayed and justified.

The strength, nature, concentration of acid centers, selective sensitivity of surfaces to gases of various electronic nature have been determined.

The system components with increased surface activity to the main gases have been recommended as materials for manufacture of appropriate measuring cells, in particular, for ammonia microimpurities.

7. References
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