Features and consistent patterns of changes in properties of the system A\textsubscript{III}B\textsubscript{V} - ZnTe solid solutions

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Abstract. By the methods developed for the InSb-ZnTe, GaSb-ZnTe systems, in the regions of mutual solubility of the initial binary compounds (InSb and ZnTe, GaSb and ZnTe), solid solutions (InSb)\textsubscript{x}(ZnTe)\textsubscript{1-x}, (GaSb)\textsubscript{x}(ZnTe)\textsubscript{1-x} have been obtained. X-ray, IR and Raman spectroscopic, electrophysical studies of the obtained solid solutions (in comparison with the initial binary compounds and among themselves) have been carried out, following the results of which the obtained solid solutions have been certified as substitutional solid solutions with a cubic sphalerite structure. The information on multicomponent diamond-like semiconductors has been expanded.

The acid-base properties of the InSb-ZnTe, GaSb-ZnTe systems components surfaces, varying in composition from weak acid to weakly basic, have been studied. General and distinctive features in the “behavior” of the InSb-ZnTe, GaSb-ZnTe systems solid solutions have been revealed. The relative influence of binary components on the type of dependences “property – composition” has been demonstrated and explained. Practical recommendations have been given for the use of solid solutions with the lowest pH\textsubscript{iso} values as materials for the manufacture of sensors for main gases trace contamination.

Keywords: solid solutions, crystal chemical, structural, optical, electrophysical, acid-base properties, features and consistent patterns of changes in properties, practical recommendations.

1. Introduction

With respect to the unique properties of the initial binary compounds (InSb, GaSb, ZnTe), including electrophysical and luminescent \cite{1} ones, it appeared promising to obtain and study multicomponent diamond-like semiconductors - solid solutions based on them as anticipated requested materials of the current, in particular, sensor technology.

The prospects lie in the possibilities of not only a controlled change in properties with a change in composition, but also in detection of unexpected, extreme effects due to complex internal processes accompanying the solid solutions formation.

Assuming that, the solid solutions of heterosystems of the A\textsubscript{III}B\textsubscript{V} - A\textsubscript{II}B\textsubscript{VI} – InSb-ZnTe, GaSb-ZnTe type, which differ in binary components of the A\textsubscript{III}B\textsubscript{V} type were chosen as a target of research. Their relative influence on the properties of solid solutions is also of interest.
2. Problem statement
As applies to the systems InSb-ZnTe, GaSb-ZnTe, to develop methods for obtaining solid solutions based on the isothermal diffusion method and known data on the physical and physical and chemical properties of the initial binary compounds.

To obtain and certify solid solutions following the results of mainly X-ray studies by appealing to the results of optical and electrophysical, mass spectrometric studies.

To establish interrelated consistent patterns in the studied volumetric and surface properties changes within specific systems and when comparing them. To use the established consistent patterns as guidelines to search for the advanced materials.

To reveal the selective sensitivity of the systems components surfaces with regard to gases of a certain electronic nature.

3. Theory
The search for new materials for semiconductor technology noticeably revived in the “era” of elementary semiconductors (mainly Si and Ge), then the attention of professionals was attracted by binary semiconductors (GaAs and others of A II B V, A II B VI type), applied in micro-, optoelectronics, nanooptoelectronics and other fields.

At present, multicomponent diamond-like semiconductors - solid solutions based on relatively studied binary semiconductors are of special interest. The feasibility is the emerging additional opportunities for obtaining materials that ensure the performance capability and stability of devices manufactured on their basis.

It is necessary to expand the range of the objects and the studied properties in order to consolidate and enrich the fundamentals for predicting and facilitating the search for the requested materials.

Interestingly, these fundamentals are based on the works by N.A. Goryunova, who thus drew the attention of instrumentation engineers first to binary and then to multicomponent diamond-like semiconductors.

In precisely this way the present paper was written.

4. Outcomes of experiments
Solid solutions (InSb) x(ZnTe)1-x (x = 95, 90, 80 mol %), (GaSb) x(ZnTe)1-x (x = 5, 10, 15, 90, 95 mol.%) were obtained using methods developed on the basis of isothermal diffusion and known data on the physical, physical and chemical properties of the initial binary compounds [1, 2]. The synthesis was carried out in the areas of their mutual solubility, in evacuated, sealed quartz ampoules, according to the temperature heating program. The completion of the synthesis, formation and structure of solid solutions were estimated by the results of X-ray studies and, indirectly, according to the results of IR spectroscopic (forbidden bandwidth determination), Raman spectroscopic, mass spectroscopic (stoichiometric composition evaluation) and electrophysical (electrical conductivity determination).

To perform the research, the end-products which are ingots at the bottom of the ampoules, were prepared in the form of powders (S = 0.3 - 0.8 m2/g) and films (d = 20-100 nm). The solid solutions as well as binary components films were prepared by discrete thermal spraying in vacuum (Tcont = 298 K, P = 1.33 10-3 Pa) onto the electrode pads of piezoelectric quartz resonators, followed by annealing in raw material vapors in the developed mode [3].

The specified molar compositions were compared with the elemental ones found subsequent to the results of electron microscopic studies [4].

X-ray studies were carried out on a D8 Advance diffractometer “Bruker” AXS (Germany) in CuKα-radiation (λ = 0.15406 nm, T = 293K) involving remote-angle survey technique [5, 6], using a Lynxeye position-sensitive detector, as well as the ICDDIPDF-2 database and TOPAS 3.0 software (Bruker), respectively, for decoding the obtained X-ray patterns and refining the lattice parameters.
**IR spectroscopic** studies were performed on a Fourier infrared spectrometer Infra-Lum FT-02 with an attachment of attenuated total internal reflection (crystal material - germanium, spectral range – 400 - 4000 cm\(^{-1}\)) and a Shimadzu spectrometer with a Fourier transformer [1]. **Raman spectroscopic** (Raman spectra) studies were carried out on a Fourier spectrometer RFS-100, with a resolution of 1 cm\(^{-1}\) [7]; **mass spectrometry** studies were conducted on the EMAL-2 laser energy-mass spectrometer [1]; **electrophysical** (electrical conductivity determination) - using the four-probe Van der Pauw method [8].

The surface properties were studied by the method of hydrolytic adsorption [9], allowing to determine the values of the hydrogen index of the isoelectric state - pH\(_{iso}\) surfaces, which characterize the average strength and the ratio of acid and basic sites. The essence of the method was to find the pH of the medium where the ampholyte adsorbents split off equal (insignificant) amounts of H\(^+\) and OH\(^-\) ions.

The components of the InSb-ZnTe, GaSb-ZnTe, (InSb\(_x\)(ZnTe)\(_{1-x}\)), (GaSb\(_x\)(ZnTe)\(_{1-x}\)) systems with distinctive isoelectric points corresponding to the minimum of solubility were used as adsorbents-ampholytes.

The reproducibility and accuracy of the experimental data were checked by the results of the parallel measurements using mathematical statistics and processing the quantitative analysis results as well as the computer programs Stat-2, Microsoft Exel and Origin.

5. Results and discussion
According to the results of X-ray, IR, Raman spectroscopic, and electrophysical studies, substitutional solid solutions with a cubic sphalerite structure are formed in the InSb-ZnTe, GaSb-ZnTe systems (at predetermined compositions). This is evidenced by the relative displacement, position and intensity distribution of the main lines in the X-ray diffraction patterns corresponding to binary components and solid solutions, smooth changes with the composition of the calculated parameter (a) values, interplanar distances (d\(_{hkl}\)), theoretical calculated crystal density (\(\rho_r\)) of crystal lattices, as well as the optical forbidden bandwidth (\(\Delta E\)) discovered on the basis of IR spectroscopic studies (by the intersection of the line tangent to the absorption edge with the h\(\nu\) axis [10]) and electrical conductivity (Figs. 1, 2).

Smooth changes in the indicated characteristics may be considered as a consequence of pairwise atomic displacement with the formation of neutral cation-anionic (donor-acceptor), uniformly distributed complexes [11], that is, solid substitutional solutions.
Figure 1. Diffraction patterns of system InSb-ZnTe (a): 1 – InSb, 2 – (InSb)$_{0.95}$(ZnTe)$_{0.05}$, 3 – (InSb)$_{0.90}$(ZnTe)$_{0.10}$, 4 – (InSb)$_{0.00}$(ZnTe)$_{0.20}$, 5 – ZnTe и GaSb-ZnTe (b): 1 – (GaSb)$_{0.95}$(ZnTe)$_{0.05}$, 2 – (GaSb)$_{0.90}$(ZnTe)$_{0.10}$, 3 – (GaSb)$_{0.15}$(ZnTe)$_{0.85}$, 4 – (GaSb)$_{0.05}$(ZnTe)$_{0.10}$, 5 – (GaSb)$_{0.05}$(ZnTe)$_{0.95}$

Figure 2. Dependences on the systems InSb-ZnTe (a), GaSb-ZnTe (b) composition of the parameter $a$ (1), interplanar space $d_{311}$ (2), theoretical calculated crystal density $\rho_t$ (3) crystal lattices, electrical conductivity $\sigma$ (4) and optical forbidden bandwidth $\Delta E$ (5)
The Raman spectra are also in consonance with the above (Fig. 3). In them, with an increase in the ZnTe content in the considered systems, a change and shift of the emission peaks is noted, which may be due to a change in the coordination environment of the initial binary compounds atoms (InSb, GaSb, ZnTe), the forbidden bandwidth and, accordingly, the formation of substitutional solid solutions [12].

The appearance in the Raman spectra of a narrow peak solid solutions (∆ν = 81-84 cm⁻¹, E = 0.01 eV) come under notice which is due to appearance as a result of the atoms substitution inside the forbidden band of discrete impurity levels between which electronic transitions occur, typical for transition metals in melting and solid solutions [13]. In addition, in the Raman spectra of solid solutions, as in the Raman spectra of antimonides, there is a strong peak related to conduction band - valence band transitions (to interband recombination) in the frequency range 2000 - 3300 cm⁻¹, the maximum position of which, with an increase in the ZnTe content, shifts towards higher frequencies (Fig. 3).

The formation of solid solutions is also indicated by the observed effect of luminescence in the anti-Stokes region when ZnTe is introduced into antimonides. The reasons for the latter were noted above: interband transitions and the appearance of impurity levels in the forbidden band during doping. Moreover, the average energies calculated based on Raman spectra corresponding to interband transitions are in good fit with the results of forbidden bandwidth determining based on IR spectroscopic studies. So, for InSb, (InSb)₀.₉₅ (ZnTe)₀.₀₅ , (InSb)₀.₉₀ (ZnTe)₀.₁₀ they are 0.22; 0.38 eV and 0.21; 0.28; 0.37 respectively.

The compositions of film samples annealed in raw material vapor at T = 550-570 K are virtually stoichiometric. Thus, as applied to the InSb-ZnTe system, they correspond to the formulae InSb₁₀₅ZnTe₁₀₄; 0.952 InSb₁₀₅ - 0.048 ZnTe₁₀₄.
The surface properties of the InSb-ZnTe, GaSb-ZnTe systems components were judged by pH values of the isoelectric state of the pH\textsubscript{iso} surfaces. After exposure to air, they fit within 6.46 - 7.70 and 6.2 - 7.70, gradually increasing in rows

\[ \text{InSb} \rightarrow (\text{InSb})_x(\text{ZnTe})_{1-x} \rightarrow \text{ZnTe} \]
\[ \text{GaSb} \rightarrow (\text{GaSb})_x(\text{ZnTe})_{1-x} \rightarrow \text{ZnTe} \]

with an increase in the ZnTe content. And thus, the surfaces properties change from weakly acidic to weakly basic.

The preferentially smooth increase in pH\textsubscript{iso} with a change in the considered systems composition (Fig. 4) additionally confirms the formation of substitution solid solutions in the considered systems.

The nature of the pH\textsubscript{iso} dependences on the composition is retained even after exposure of the system components to a CO atmosphere. In this case, the pH\textsubscript{iso} values shift to the alkaline region, which is logical to associate with the electronic structure and the dual function of CO molecules [14].

![Figure 4](image.png)

**Figure 4.** Dependencies on the composition of the systems InSb-ZnTe (a), GaSb-ZnTe (b) components of pH isoelectric state of the surface after exposure to air (1) and in carbonous oxide atmosphere (2)

Having an excess electron density due to the lone electron pairs of carbon and oxygen atoms as well as due to the formation of a double bond between them, CO can represent a Lewis base (donor of electron pairs), entering into reaction according to the donor-acceptor mechanism. At the same time, the surfaces of the InSb-ZnTe, GaSb-ZnTe systems components contain coordination-unsaturated atoms (in particular, In, Ga, Zn), which, lacking electrons, exhibit the properties of Lewis acids (acceptors of electron pairs). As a result of the interaction of CO lone electron pairs and vacant orbitals of coordination-unsaturated atoms, Lewis acid sites on the surfaces are partially extinguished. That leads to a shift in pH\textsubscript{iso} to the alkaline region.

A comparative analysis of the solid solutions properties of the InSb-ZnTe, GaSb-ZnTe systems containing a common binary component of the A\textsuperscript{III}B\textsuperscript{VI} (ZnTe) type and differing in the binary components of the A\textsuperscript{III}B\textsuperscript{V} (InSb and GaSb) type was of apparent interest. This will be discussed further.

6. Results and discussion
As a result of a comparative analysis of the properties within each considered system and when comparing in different systems, it was possible to identify common and distinctive features.

Common features include
- formation of substitutional solid solutions with a cubic structure of sphalerite in the systems;
- with an increase in the ZnTe content, smooth changes in the parameter (a) values, interplanar distances (dhkl), forbidden bandwidth (∆E), electrical conductivity (σ), change in the relative intensity, broadening and shift of peaks in the Raman spectra;
- smooth changes in pHiso with a transition from weak-acid regions to weak basic ones.

Here the attention should be paid to the regular confirmation of our considerations on the influence on the nature of changes in the solid solutions properties of the difference in the binary compounds properties values such as the melting point (Tm), electronegativity difference (∆x), forbidden bandwidth (∆E) (for example, [4]).

As applied to the considered systems, in accordance with the above, mainly smooth changes in the solid solutions properties in the composition are observed with noticeable differences in the initial binary compounds properties.

So, Tm, ∆x, ∆E are:
- for InSb and ZnTe 525 and 1295°C; 0.10 and 0.5; 0.18 and 2.12–2.27 eV
- for GaSb and ZnTe 710 and 1295°C; 0.20 and 0.5; 0.72 and 2.12–2.27 eV.

The distinctive features include unequal contents of the binary component ZnTe in solid solutions, at which neutral states of their surfaces occur: for the InSb−ZnTe system - at 15 mol. %, for the GaSb-ZnTe system - at 95 mol. %.

This corresponds to large differences in the values of ∆E, ∆x of the binary components of the InSb-ZnTe system (they are 2.09 eV and 0.4), compared with those in the GaSb-ZnTe system (they are 1.55 eV and 0.3). In this case, even at a low content of ZnTe, its effect on the InSb-ZnTe system solid solutions surfaces state is noticeable.

According to our long-term observations (for example, [11]), the most acidic surfaces exhibit increased activity with respect to basic gases.

Accordingly, the solid solutions of the InSb-ZnTe, GaSb-ZnTe systems with the lowest pHiso values can be recommended for the manufacture of sensors for main gases trace contamination.

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