Obtaining, bulk physical and chemical properties, certification of heterosystem InSb-ZnS solid solutions

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Abstract. Solid solutions (InSb)ₓ(ZnS)₁₋ₓ of different compositions have been obtained using a specially developed technology (applied to the InSb-ZnS system under study). Performed X-ray and electron-microscopic studies made it possible to certify the solid solutions obtained as solid substitutional solutions with the sphalerite structure, and also to determine their element composition, which practically coincides with the molar composition.

The influence of the physical and chemical properties of the initial binary compounds on the corresponding physical and chemical properties of the solid solutions has been shown (with the example of two A⁺III'B⁺V - A⁺II'B⁺VI type systems) which manifested in their concentration dependences nature.

The inevitable competition between the relative contributions of Lewis and Bronsted acidic sites has been justified.

The predictions of the trend of the surface isoelectric state pH in the series InSb → (InSb)ₓ(ZnS)₁₋ₓ → ZnS and their activity with respect to gases of a certain electronic nature have been given.

Keywords: solid solutions, physical and chemical properties, certification, promising materials, semiconductor gas analyzers.

1. Introduction

The research subjects in the present work are solid solutions of the new heterogeneous replacement (type A⁺III'B⁺V - A⁺II'B⁺VI) -InSb-ZnS system.

The unique physical and physicochemical properties of the initial binary compounds (InSb, ZnS), the possibility of adjusting and optimizing properties with a change in composition and the discovery of unexpected effects due to the peculiarities of internal processes accompanying the formation of solid solutions allow to expect to obtain promising materials for sophisticated technology and semiconductor instrument engineering, including semiconductor gas analyzers [1, 2].

To accelerate the realization of the expected prospects it is necessary to develop a relatively simple technology for obtaining and knowing their bulk and surface physical and chemical properties.

In terms of the above, at the first stage, the results of obtaining, X-ray, electron microscopic studies and certification of InSb-ZnS system solid solutions are analyzed relying on necessary information on a single-type system (GaSb-ZnTe).

2. Problem statement
To develop the technology, to obtain InSb-ZnS system solid solutions certification based on the results of X-ray studies. With the help of electron microscopic studies to determine their elemental composition, surface structure.

Using the example of two systems of the type A^{III}B^{V}-A^{II}B^{VI} (InSb-ZnS, GaSb-ZnTe), it is necessary to observe the influence of the physical and chemical properties of the initial binary compounds on the same physical and chemical properties of the formed solid solutions and the nature of the “property-composition” dependences.

To evaluate the relative contributions of Lewis and Bronsted sites and justify the inevitable competition between them.

To predict the nature of the change in the pH_{iso} in the InSb → (InSb)_{x} (ZnS)_{1-x} → ZnS series and, accordingly, the surfaces activity towards gases of a certain electronic nature.

3. Experimental part

The investigated objects were mainly fine powders InSb, ZnS and their solid solutions (InSb)_{x} (ZnS)_{1-x} (x = 0.04, 0.08, 0.18, 0.23, 0.90, 0.95, 0.98 mol). The solid solutions were prepared using a special technology (relative to the InSb-ZnS system), based on the isothermal diffusion of InSb, ZnS (in vacuumed, sealed quartz vessels, at a reasonably selected temperature of 1000 K), using a special program of temperature heating [2]. The completion of the synthesis was concluded from the results of X-ray diffraction studies used for the certification, structure determination and the basic structural characteristics of solid solutions. The results of X-ray studies were supplemented by the results of electron microscopy studies.

X-ray studies were carried out on the D8 Advance diffractometer of Bruker (Germany) in CuKα radiation (λ = 0.15406 nm, T = 293 K) using the large-angle survey technique [3, 4] and the Lynxeye position-sensitive detector. The decoding of the obtained X-ray diffraction patterns was carried out using the powder diffraction database ICDDPDF-2, refinement of the lattice parameters in the TOPAS 3.0 program (Bruker), using the least squares method.

Electron microscopical study was performed on a scanning electron microscope SCM – 5700, equipped with a nitrogen-free x-ray energy-dispersive spectrometer [5].

The reproducibility and accuracy of the data was verified by the results of parallel measurements using mathematical statistics and processing the results of quantitative analysis. Statistical processing of the obtained numerical values, calculation of measurement errors, construction and processing of graphical dependencies were carried out using computer programs Stat-2, Microsoft Excel and Origin.

4. Results and discussion

Let us consider the results of X-ray studies (fig. 1, 2, table 1). They indicate the formation of solid substitutional solutions with the cubic structure of sphalerite in the InSb-ZnS system. The relative position and distribution of the intensities of the main lines on the x-ray diffraction patterns of binary compounds and solid solutions, the dependence on the composition of the values of the parameter of the crystal lattices (a), the interplanar distances (d_{hkl}), and the density (ρ) served as criteria. Deviations from the smooth or linear dependencies a = f (x_{ZnS}), d_{hkl} = f (x_{ZnS}) at the boundary content in the ZnS system (77 mole %), still “allowing” unlimited mutual solubility of the binary components (InSb, ZnS), i.e. formation of solid substitution solutions can be explained by not manifested structure change [2, 6].
**Figure 1.** X-ray diffraction patterns diagrams of the InSb-ZnS system components: 1 – InSb, 2 – InSb$_{0.98}$ZnS$_{0.02}$, 3 – InSb$_{0.95}$ZnS$_{0.05}$, 4 – InSb$_{0.90}$ZnS$_{0.10}$, 5 – InSb$_{0.25}$ZnS$_{0.75}$, 6 – InSb$_{0.18}$ZnS$_{0.82}$, 7 – InSb$_{0.08}$ZnS$_{0.92}$, 8 – InSb$_{0.04}$ZnS$_{0.96}$, 9 – ZnS.
Table 1. Crystal lattice parameters value ($a$), interplanar distances ($d_{hkl}$) and theoretical calculated crystal density ($\rho_r$) of InSb-ZnS system components.

| X (Mole fraction ZnS) | $a$, Å | $d_{hkl}$, Å | $\rho_r$, r/cm$^3$ |
|----------------------|--------|--------------|-------------------|
|                      |        | 111          | 220               | 311               |                           |
| 0                    | 6.4770±0.001 | 3.7411 | 2.291 | 1.9550 | 5.7820 |
| 0.02                 | 6.4583±0.001 | 3.7287 | 2.287 | 1.9518 | 5.7571 |
| 0.05                 | 6.4507±0.001 | 3.7243 | 2.286 | 1.9514 | 5.6745 |
| 0.10                 | 6.4462±0.001 | 3.7217 | 2.283 | 1.9500 | 5.5140 |
| 0.77                 | 5.3970±0.001 | 3.1160 | -     | 1.6303 | 5.4620 |
| 0.82                 | 5.4020±0.001 | 3.1191 | -     | 1.6305 | 5.1530 |
| 0.92                 | 5.4033±0.001 | 3.1296 | -     | 1.6307 | 4.5654 |
| 0.96                 | 5.4041±0.001 | 3.1202 | -     | 1.6310 | 4.3879 |
| 1                    | 5.4107±0.001 | 3.1239 | -     | 1.6314 | 4.0914 |
**Figure 2.** Dependence on the composition of the crystal lattices parameter values $a$ (2), interplanar distance $d_{111}$ (1), and theoretical calculated crystal density $\rho_c$ (3) of the InSb-ZnS system components.

Solid solutions formation is also indicated by the absence of additional lines on the X-ray patterns corresponding to unreacted binary components and blurriness of the main lines. *Based on the results of electron microscopic studies* (fig. 3–5), the elemental compositions of binary components and solid solutions, the structure of surfaces, the average particle size, the dependence of the number of particles of a certain (average) size on the composition of the system have been determined.

**Figure 3.** SEM - image of InSb powder in phase contrast regime.
It is established [7]: the elemental composition of all components has a satisfactory agreement with the mole composition, surfaces have a polycrystalline structure with an inhomogeneous distribution of crystallites that can be associated with agglomerates from grains of various sizes.

In our opinion, it was interesting to follow how physical and chemical properties of the initial binary compounds – $A_{III}B_{V}$-$A_{II}B_{VI}$ type system components – affect on the same properties of the formed solid solutions and the dependence of the latter on the systems composition. Let us demonstrate it with the example of two systems: InSb-ZnS and GaSb-ZnTe (tables. 1, 2, fig. 2, 6).

More significant differences in the values of the indicated physical and chemical properties of the binary components of the InSb-ZnS system are noticed rather than the binary components of the GaSb-ZnTe system (table 2). As a result we have an extreme in the first case and the smooth in the second one dependences $a = f (x_{A2B6})$, $d_{hkl} = f (x_{A2B6})$ (fig. 2, 6).
Table 2 Basic physico-chemical properties of initial binary components of InSb-ZnS, GaSb-ZnTe systems.

| The binary component of systems | Crystal lattice type | Crystal lattice parameter ($a$, Å) | Density, ($\rho_r$, g/cm$^3$) | Melting temperature ($T_m$, °C) | Bandgap width ($\Delta E$, eV) | Electronegativities difference ($\Delta X$) |
|--------------------------------|----------------------|-----------------------------------|-----------------------------|-------------------------------|-------------------------------|---------------------------------|
| InSb                           | Sphalerite           | 6.4779                            | 5.7820                      | 525                           | 0.18                          | 0.10                            |
| ZnS                            | Sphalerite           | 5.4107                            | 4.0914                      | 1830                          | 3.67                          | 0.90                            |
| GaSb                           | Sphalerite           | 6.096                             | 5.650                       | 710                           | 0.72                          | 0.20                            |
| ZnTe                           | Sphalerite           | 6.108                             | 5.668                       | 1295                          | 2.12-2.20                     | 0.50                            |

Figure 6. Dependence on the composition of the crystal lattices parameters values $a$ (1), interplanar distance $d_{111}$ (2), and theoretical calculated crystal density $\rho_r$ (3) of the system GaSb-ZnTe components.

It should also be noted the density ($\rho_r$) decreases smoothly with an increase in the content of zinc sulphide in the InSb-ZnS system with parallel smooth increases in the band gap ($\Delta E$) and the difference in electronegativity ($\Delta X$) (fig. 2, table 2).

So, we have the case of the inevitable competition between the growth of the coordination unsaturation of surface atoms, contribution of Lewis sites and increase in the bond ionicity, degree of surface hydration and accordingly the contribution of the Bronsted sites. With the predominance of the latter, the hydrogen index of the surfaces isoelectric state ($pH_{iso}$) in the InSb $\rightarrow$ (InSb)$_x$(ZnS)$_{1-x}$ $\rightarrow$ ZnS series should be expected to increase.
5. Conclusions
According to the developed technology solid solutions of the InSb-ZnS system certified on the basis of the results of X-ray studies as solid substitution solutions with a sphalerite structure have been obtained.

As a result of electron microscopic studies the elemental composition of the InSb-ZnS system components have been determined, practically coinciding with the molar composition; polycrystalline structure of surfaces has been established.

The influence of the initial binary components physical and chemical properties on the same physicochemical properties of the formed solid solutions has been shown by the example of two systems of $A^{III}B^V$-$A^{II}B^{VI}$ (InSb-ZnS, GaSb-ZnTe) type which manifested in the extreme and smooth character of the dependences $\alpha = f (x_{A2B6})$, $D_{hk\ell} = f (x_{A2B6})$ respectively for the InSb-ZnS and GaSb-ZnTe systems.

The inevitable competition on the surfaces of the InSb-ZnS system components between the relative contributions of Lewis and Bronsted acid sites has been proved. Predictions have been made about the nature of the pH of the pH in the InSb $\rightarrow$ (InSb)$_x$(ZnS)$_{1-x}$ $\rightarrow$ ZnS series, and hence about the surface activity of gases with certain electronic nature.

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