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Mechanochemical synthesis and physico–chemical investigations of new materials for gas sensors

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Abstract. Solid solutions of the InSb-ZnTe semiconductor system containing up to 20 mol.% of ZnTe were synthesized for the first time. The role of mechanochemical treatment in the process of obtaining solid solutions of this system is shown. Solid solutions in the InSb-ZnTe system have been identified by Raman spectroscopy, and the optical properties of its components have been studied. On the basis of an analysis of the anti-stokes spectral radiation distribution the solid solutions formation was identified both on the dependence of the spectral distribution maximum's shift on the composition of the InSb<sub>1-x</sub>-ZnTe<sub>x</sub> system, and by estimating the radiation intensity of the initial binary semiconductors at frequencies corresponding to the LO- and TO- vibrations of the binary compounds crystal lattice. The values of the band gap for InSb, (InSb)<sub>0.95</sub>(ZnTe)<sub>0.05</sub> and (InSb)<sub>0.9</sub>(ZnTe)<sub>0.1</sub> were calculated, their values were 0.22 eV, 0.30 eV and 0.38 eV, respectively.

1. Introduction
Interest in solid solutions based on indium antimonide and zinc telluride is primarily associated with their unique electron-optical properties, which makes it possible to obtain promising materials with controlled electronic and other physicochemical properties.

Using the A<sup>2</sup>B<sup>5</sup> and A<sup>2</sup>B<sup>6</sup> type compounds and solid solutions based on them as components of the sensor element provides a sensitivity to a broad range of toxic and chemically-active gases in the environment and gas emissions [1–6]. The basis of semiconductor sensors are thin layers (250 nanometers) InSb, ZnTe and their solid solutions deposited on appropriate substrates. Selection of sensitive material for semiconductor sensors represents obtain samples of different composition, and studying the sensitivity of their surface in adsorption different gases [4]. The main difficulty in obtaining and investigating solid solutions is the duration and laboriousness of the isothermal diffusion method used in their synthesis. Therefore, the development of new approaches to the complex multicomponent solid solutions’s synthesis is a needed task.

In work solid solutions were synthesized from mixtures of initial components (InSb and ZnTe powders), taken in certain molar ratios. Preliminary mechanochemical treatment of the binary semiconductors starting mixtures preceded the process of their alloy. Mechanochemical treatment contributes to the emergence of new active sites on the freshly formed solids surface and to acceleration of diffusion processes. As a result, it allows to increase the reactivity of substances and to intensify the course of solid-phase reactions [7].

The optical properties of the synthesized samples were studied whith using the Raman spectroscopy method (Raman scattering method). Based on the frequencies's values of the crystal lattice vibration, both the binary components of the four-component semiconductor system and the obtained solid solutions were identified. In work the band gap was calculated both for the initial
compounds and for solid solutions. In addition, Raman spectroscopy method provides the possibility of obtaining information not only about the states within the forbidden band, which is especially important in the case of doping, but also the types of atoms and their coordination environment, which determines their reactivity [8, 9].

2. Experimental
Optical studies of the initial binary compounds and synthesized samples of solid solutions were carried out by Raman spectroscopy method on the RFS-100 Fourier spectrometer, with a resolution of 1 cm\(^{-1}\). The samples were excited by laser radiation at room temperature (yttrium-aluminum garnet with neodymium YAG:Nd\(^{3+}\) (\(Y_3Al_5O_{12}:\text{Nd}^{3+}\)), \(\lambda = 1064\) nm). The obtained data were analyzed in the anti-stokes scattering region in the observation range 0 – 4000 cm\(^{-1}\) and in a narrow range of crystal lattice frequencies (0 – 400 cm\(^{-1}\)).

On the basis of an analysis of the anti-stokes spectral radiation distribution the solid solutions formation was identified both on the dependence of the spectral distribution maximum's shift on the composition of the InSb\(_{1-x}\)-ZnTe\(_x\) system, and by estimating the initial binary semiconductors radiation intensity at frequencies corresponding to the LO- and TO- vibrations of the binary compounds crystal lattice.

The experimental data, their reproducibility and accuracy was monitored by parallel measurements, and the use of computational algorithms of mathematical statistics.

3. Results and considerations
The results of the spectral distribution of the anti-stokes and stokes radiation of the four-component solid solutions system InSb\(_{1-x}\)-ZnTe\(_x\), exposed in air, are shown in Figures 1 and 2.

The obtained dependences show that in the spectra of the starting compounds in the anti-stokes region there are narrow peaks corresponding to the LO and TO frequencies of their oscillations crystal lattice: 180 cm\(^{-1}\) and 191 cm\(^{-1}\) for indium antimonide; 206 cm\(^{-1}\) (LO-component) and 177 cm\(^{-1}\) (TO-component) for zinc telluride.

Analysis of the spectra presented above showed, that the peak, defined as the peak of the interband recombination (corresponding to the transition "conduction band - valence band"), is present both in the spectrum of indium antimonide and in the spectra of synthesized solid solutions, and is fixed in the frequency range 2500 – 3300 cm\(^{-1}\) [9]. The difference between solid solutions and starting compounds is manifested in its intensity as well as the position of the maximum, which shifts to higher frequencies with increasing zinc telluride content.

Strong exciton absorption is characteristic of A\(^2\)B\(^6\) compounds [8], therefore the certain amount of ZnTe contained in a InSb at the formation of solid solutions causes the observed luminescence effect in the anti-stokes region. As mentioned above, it is due to, firstly, to the appearance of impurity levels in the band gap of indium antimonide by reason of the doping, and, secondly, due to interband transitions.
In addition, analysis of Raman spectra (Figure 1) made it possible to establish that at the stage of mechanochemical treatment of the initial mixture of binary components InSb and ZnTe, partial formation of solid solutions is occurred. This is confirmed by the optical vibrations of initial components lattices are presented not only in the spectrum of the mechanical mixture, in addition, in the spectrum of the mechanoactivated mixture \( \text{InSb}_{1-x}\text{ZnTe}_x \) (where \( x = 0.05 \)) as well as in the spectrum of a solid solution with the same concentration of ZnTe. The presence in spectrum of mechanoactivated mixture \( \text{InSb}_{1-x}\text{ZnTe}_x \) (where \( x = 0.05 \)) in the range 2500 – 3500 cm\(^{-1}\) a broad band of low intensity indicates that the synthesis of solid solutions at the stage of mechanochemical treatment occurred in part.

**Figure 1.** Raman spectroscopy: 1 – InSb; 2 – \( \text{InSb}_{1-x}\text{ZnTe}_x \) – mechanical mixture; 3 – \( \text{InSb}_{1-x}\text{ZnTe}_x \) – solid solution, where \( x = 0.05 \) (5 mol.%).
Figure 2. Raman spectroscopy: 1 – InSb$_{1-x}$ZnTe$_x$ solid solution, where $x = 0.05$ (5 mol.%); 2 – InSb$_{1-x}$ZnTe$_x$ solid solution, where $x = 0.10$ (10 mol.%); 3 – ZnTe.

The mean energies corresponding to the interband transitions were calculated on the basis of Raman spectra. The calculated values correspond to the band gap width and make up 0.22 eV, 0.30 eV and 0.38 eV for InSb, (InSb)$_{0.95}$(ZnTe)$_{0.05}$ and (InSb)$_{0.9}$(ZnTe)$_{0.1}$ respectively and vary linearly depending on the solid solutions composition. When forming unbroken row of substitutional solid solutions, the most of the parameters are linear function of composition, and that fact confirms the formation in InSb$_{1-x}$ZnTe$_x$ solid solutions of cation-anion complexes distributed uniformly [1, 2, 8, 9].

4. Summary
Solid solutions of the InSb-ZnTe semiconductor system containing up to 20 mol.% of ZnTe were synthesized for the first time. The role of mechanochemical treatment in the process of obtaining solid solutions of this system is shown. Solid solutions in the InSb-ZnTe system have been identified by Raman spectroscopy (Raman scattering method), and the optical properties of its components have been studied.
Further study of the semiconductor multicomponent solid solutions surface properties in real conditions will allow us to identify samples that have the greatest sensitivity to toxic microimpurities and to develop recommendations for their use as sensitive elements of gas sensors and sensory arrays.

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