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The activity of new materials surfaces - ternary semi-conductors with cationic and anionic substitution

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Abstract

The article describes the synthesis of solid solutions of ZnS-CdSe, ZnS-CdS, ZnS-ZnTe systems (for the first time in the given compositions). Through X-ray, IR-spectroscopic and electron-microscopic studies, the findings about their bulk physicochemical properties were obtained. These data can be used for certification and determination of their structures. It was determined that solid substitution solutions with preliminary hexagonal structures are formed. According to the results of the acid-base properties investigation, the surfaces of all stated systems components exposed to air have slightly acid nature and offer the increased activity against the basic gases. Generally, the coordinatively unsaturated atoms account for the surfaces acidity.

The interrelated laws were found in changing of the acid-base and most essential bulk physicochemical properties on modifying the composition of the series of analogues ZnBIV, CdBIV and the solid substitution solutions formed by them. These laws likely connected to the electron structure of the non-metallic components are used to find the most active adsorbents, primary transducer materials of the sensors for basic gases micro-impurities.

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1. Introduction

The parameters of semi-conductor devices and units are largely dependent on both the used material composition and the surfaces state and the processes at the media border. Consequently, the projected development of unknown

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ternary crystal-like semi-conductors and the investigation of the surface properties are relevant in the scope of the specified problem.

2. Study subject

The research is aimed at the fine powders of ZnS, CdSe, CdS, ZnTe and solid solutions \((ZnS)_{\alpha}(CdSe)_{1-\alpha}\); \((ZnS)_{\alpha}(CdS)_{1-\alpha}\); \((ZnS)_{\alpha}(ZnTe)_{1-\alpha}\) of different compositions. The solid solutions were received based on the method of isothermal diffusion of the binary compounds (ZnS and CdSe, ZnS and CdS, ZnS and ZnTe) in vacuum-sealed quartz vessels at the temperature of \(1173^\circ K\) [1]. The mode of obtaining the solid solutions corresponded to the developed thermal heating programme. The sample weights of the initial binary compounds with the required molar ratio were preliminary dispersed, or activated mechanochemically. The end-products were dense polycrystalline ingots at the bottom of the vessel. The end of the synthesis was determined by the results of X-ray analysis, later used for the certification, together with the results of IR-spectroscopic and electron-microscopic studies, and the determination of the solid solutions structures.

3. Methods

X-ray analysis was conducted on the diffractometer D8 Advance of the company "Bruker" (Germany) in CuKα radiation (\(\lambda=0,15406\) nm, \(T=293^\circ K\)) according to the method of high-angle scattering [2] with the use of position-sensitive detector Lynxeye.

The interpretation of the resulting radiographs (diffractograms) was conducted with the help of the powder diffraction database ICDD PDF-2. The adjustment of the lattice parameters was performed by the least square method on software TOPAS 3.0 (Bruker).

IR-bands were recorded on FT-IR spectrometer InfraLUM FT-02 with adaptor MFTIR [3].

Electron-microscopic studies were performed on the scanning electron microscope JCM-5700 equipped with the nitrogen-free X-ray energy-dispersive spectrometer [4].

Acid-base properties of the surface were investigated by the hydrolytic adsorption technique (the determining of isoelectric state \(pH - pH_{iso}\), mechanochemistry, nonaqueous conductometric titration and MFTIR IR-spectroscopy [1,5,6].

4. Results and discussion

According to X-ray studies, the solid substitution solutions are formed in the systems ZnS-CdSe, ZnS-CdS, ZnS-ZnTe (with the specified compositions, mol.%). The corresponding lines on the radiographs are shifted against the binary components lines with their number being constant (Fig. 1). The dependence of the values of the lattice parameters \((a,c)\), inter-planar spacing \((d_{hkl})\) and areal density \((\rho)\) on the systems compositions is of smooth nature (Fig. 2).
Fig. 1. Radiographs of CdSe-ZnS systems components: 1. - ZnS; 2. - (ZnS)0.39(CdSe)0.61; 3. - (ZnS)0.23(CdSe)0.77; 4. - CdSe

Fig. 2. The dependence of the parameters values of the crystal lattice a (2), c (1) and areal density ρr (3) of CdSe-ZnS system components on the composition
According to the position and allocation after the basic lines intensity, the systems components have mainly hexagonal wurtzite structure.

IR-spectroscopic studies (Fig. 3) allow to determine the chemical composition of the system components initial (real) surface and to find the definite laws in the changes of a relative position and basic IR absorption bands intensity together with the composition modification. The surface chemical composition, just like the other crystal-like semiconductors [1], mainly contains absorbed water molecules, hydroxyl groups, carbon-containing compounds and surface atoms oxidation products. As for the laws in the relative position changes and IR-bands changes after the systems composition modification, they are the most obvious in the example of the absorbed molecules CO2 and H2O stretching bands (Fig.3). This fact adds to the proof of the solid substitution solutions formation and, with the other information included, can be used in estimating the acid-base properties and choosing effective materials and adsorbents.

Electron-microscopic studies allowed to determine the ultimate compositions of the solid solutions and systems binary components, and their surface structure.

The investigation of the acid-base properties of the surface (Fig. 4) demonstrates that pH values of the isoelectric state (pHiso) of the surface exposed to air correspond mainly to the slightly acid area (varying from 6.35 to 7.10) and, consequently, indicates the prevalence of acid sites and the expected increased activity against the basic gases [1,6]. According to the results of the mechanochemical studies and nonaqueous conductometric titration, coordinatively unaturated surface atoms act as the acid sites.
5. Conclusion

The found laws are of great importance. The binary components of the solid solutions based on the pH\textsubscript{iso} values are arranged in a row ZnS, CdS, CdSe, ZnTe (6.35; 6.5; 6.84; 7.1). In other words, zinc sulfide has a more acid surface than the other chalcogenides. It is of interest that the bandgap decreases in the same order (3.67; 2.42; 1.88; 2.2). The highlighted tendencies are likely to be connected with the electron structure of the metalloid components of these compounds and they were bound to affect the surface acidity of the solid solutions (ZnS)\textsubscript{x} (A\textsuperscript{II}B\textsuperscript{VI})\textsubscript{1-x}.

The mentioned laws, the definite interrelation of the acid-base and bulk physicochemical properties of the investigated systems properties, and their increased absorption activity against the basic gases are to be used to find the most active adsorbents, primary transducer materials of the sensors for basic gases micro-impurities.

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References