Multicomponent system of heterogeneous substitution
InP-CdTe. Preparation, attestation. Volume properties

I A Kirovskaya, E V Mironova, A O Murashova, R V Ekkert and I Yu Umanskiy
Omsk State Technical University, 11, Mira Ave., Omsk, 644050, Russian Federation

Abstract. Using the isothermal diffusion method, improved with the consideration of physical and physicochemical properties of the initial binary compounds (InP, CdTe), solid solutions (InP)x(CdTe)1-x, were obtained, certified according to X-ray, submicroscopical and microscopical studies as substitution solid solutions with sphalerite structure. The consistent patterns were revealed in the compositional changes of bulk properties (crystallochemical, structural) which have both gradual and extreme nature.

The constitutional diagrams “property – composition” were plotted. Certain correlations were found between them, which became the principle of practical guidelines for facilitating the search for advanced materials for measuring cells.

Keywords - solid solutions, advanced materials, bulk properties, consistent patterns, measuring cells.

1. Introduction
The present work is concerned with searching for advanced materials for sophisticated, in particular, sensor technology, which includes both an expansion of the research objects range and knowledge of their bulk and surface properties.

Multicomponent diamond-like semiconductors - solid solutions based on binary compounds of $\text{A}^{\text{III}}\text{B}^\text{V}$-$\text{A}^{\text{II}}\text{B}^\text{VI}$ type seem to be prospective targets. With the change in their composition, it is possible not only to change the properties predictably, but also by virtue of complex internal processes of solid solutions formation, to detect unexpected properties that are particularly attractive in scientific and practical aspects.

The InP-CdTe system was chosen, individualized by its originality: when the types of initial binary compounds (AIIIBV и AIIIBVI) differ, the similarity of characteristics such as melting point (1070°C and 1090°C), electronegativity difference (0.4 and 0.4), forbidden bandwidth (1.35 and 1.51 eV) comes under notice. For that reason, the forthcoming competition between statistical and extreme factors in the properties changes with a change in the system composition [1, 2] may act as an announcement.

2. Problem statement
Using the improved method of isothermal diffusion of the initial binary compounds InP, CdTe to obtain solid solutions of the InP-CdTe system.

To perform X-ray, submicroscopical studies required for certification, determination of the structure of the obtained solid solutions as well as for broadening awareness of the multicomponent diamond-like semiconductors properties.

To establish interrelated consistent patterns in the changes of the studied properties with a change in the system composition, to plot the constitutional diagrams “property-composition”. To give findings
on the possibility of their usage for easier search for the advanced materials with sequential practical guidelines.

3. Theory
The systems of the $\text{AIIIBV-AIIBVI}$ type, the representative of which is the system under study (InP-CdTe), represent a new type of heterovalent substitution: cationic and anion-formers with unequal valence are in different Mendeleev's groups. The nature of the interatomic bonds (tetrahedral covalent links) and as a consequence, the crystal structure identity is common for these compounds. In solid solutions of heterovalent substitution unlike isovalent substitution solid solutions, the substituting atoms in the parent lattice behave as electrically active impurities. This logically leads to the main substance doping and with increase in the content of the second component it leads to the crystal lattice change and, as a result, to the change in the physical and physicochemical properties of solid solutions.

Taking into account the above mentioned and the complexity of internal processes accompanied by solid solutions formation [1], with a change in their composition, changes in the properties not only according to the statistical law but also extreme ones are expected. The latter are of particular interest as regards of searching for advanced, effective materials for sophisticated technology and specifically for sensor technology, semiconductor gas analysis, semiconductor catalysis.

This fact, taking into account the undeniable importance and necessity of carrying out fundamental research, determined the practical aspect of the present work.

4. Experimental part
The solid solutions $(\text{InP})_x(\text{CdTe})_{1-x}$ $(x=0.09, 0.12, 0.16, 0.18)$ were obtained using the improved (with regard to the system) method of isothermal diffusion of initial binary compounds (InP, CdTe) in previously justified modes, according to specific program of temperature heating [1, 3]. They were certified in accordance with the results of X-ray, submicroscopical and microscopical studies; solid solutions and binary components were used for the research in the form of fine powders ($S_{sp} = 0.34 – 1.2$ $m^2/g$).

X-ray studies were carried out on the Advance D8 Powder X-ray Diffractometer manufactured by BRUKER AXS (CuK$\alpha$- radiation, $\lambda = 0.154056$ nm, $T=293K$), involving wide-angle survey technique [4-6], using position-sensitive detector Lynxeye, submicroscopical studies were performed with a scanning electronic microscope JCM-5700, equipped with an attachment for energy-dispersive analysis JED 2300 [7]; microscopical studies were conducted using the Micromed POLAR 3 microscope.

Reproducibility and accuracy of the experimental data were checked based on the parallel measurements results involving mathematical statistics, quantitative analysis results processing methods and computer programs Stat-2, Microsoft Excel and Origin.

The results of the performed studies are presented in Fig. 1-4 and in Table 1.2.

5. Results and discussion
The results of X-ray studies given Fig.1, 2 and Table 1 demonstrate the substitution solid solutions formation in the InP-CdTe system: on the X-ray patterns, the lines accounting for solid solutions are shifted relative to the initial binary compounds lines (InP, CdTe) at constant number of them; dependence of the parameter estimated value (a), crystal lattices interplanar distances ($d_{hkl}$) on the composition have a smooth, near-linear nature.

Deviation of the dependence $\rho_r = f (X_{\text{CdTe}})$ from Vegard's law is attributable to the influence of the inhomogeneous distribution of cationic anionic complexes [8]. The results of submicroscopical and microscopical studies, indicating the polycrystal structure of the InP-CdTe system components with an inhomogeneous crystal distribution (Fig. 3) correspond to that.
The full completion of solid solutions synthesis is confirmed by the absence of additional lines on the X-ray patterns accounting for unreacted binary components and blurring of the base lines.

Figure 1. Line X-ray pattern of the system InP-CdTe components: 1 – InP, 2 – (InP)\textsubscript{0.18}(CdTe)\textsubscript{0.82}, 3 – (InP)\textsubscript{0.16}(CdTe)\textsubscript{0.84}, 4 – (InP)\textsubscript{0.12}(CdTe)\textsubscript{0.88}, 5 – (InP)\textsubscript{0.09}(CdTe)\textsubscript{0.91}, 6 – CdTe

Table 1. Parameter values of crystal lattice (\(a\)), interplanar distances (\(d_{\text{hkl}}\)) and theoretical calculated crystal density (\(\rho_t\)) of the system InP-CdTe components
| X_{CdTe}, Mole fraction CdTe | Crystal lattice type | \( a, \AA \) | d_{hkl}, \AA | \( \rho_r, \text{g/cm}^3 \) |
|-------------------------------|---------------------|--------------|----------------|-----------------|
| 0                            | cub.                | 5.89 ± 0.001 | 3.40252        | 1.77590 –       | 4.7312          |
| 0.82                         | cub.                | 6.340 ± 0.001| 3.66024        | 2.24713         | 5.8137          |
| 0.84                         | cub.                | 6.344 ± 0.001| 3.66311        | 2.24683         | 5.8513          |
| 0.88                         | cub.                | 6.371 ± 0.001| 3.67841        | 2.25697         | 5.8734          |
| 0.91                         | cub.                | 6.403 ± 0.001| 3.69730        | 2.26366         | 5.8577          |
| 1                            | cub.                | 6.481 ± 0.001| 3.7280         | 2.28136         | 5.8545          |

**Figure 2.** Dependence on the parameter values composition \((a) – 1,\) interplanar distances \((d_{hkl}) – 3\) of crystal lattices and theoretical calculated crystal density \((\rho_r) – 2\) of the system InP-CdTe components.

The base lines position on the X-ray patterns, their distribution by intensity (Fig. 1) indicate the cubic structure of sphalerite in all components of the \((\text{InP, CdTe}, (\text{InP})_x(\text{CdTe})_{1-x})\) system.
Based on submicroscopical studies (Fig. 3), the elemental composition, surface structure, average sizes ($d_{av}$) and average numbers ($n_{av}$) of the most displayed solid solution particles and binary components of the InP-CdTe system were determined.

Figure 3. SEM – images of InP ($a$), (InP)$_{0.18}$(CdTe)$_{0.85}$ ($b$), (InP)$_{0.16}$(CdTe)$_{0.84}$ ($c$), (InP)$_{0.12}$(CdTe)$_{0.88}$ ($d$), (InP)$_{0.09}$(CdTe)$_{0.91}$ ($e$), CdTe ($f$) powders.

The elemental compositions basically coincide with the specified molar compositions; the surfaces, as previously noted, are polycrystalline with inhomogeneous distribution of the crystals capable to lump...
into agglomerates from various size grains (Fig. 3), the average numbers of the most displayed particles are in accordance with their average sizes (Table 2).

The results of microscopical studies correspond to the results of submicroscopical studies: the surface structure, average sizes ($d_{av}$), average numbers ($n_{av}$) of the most displayed particles, determined basing on microscopic images (see, for example, [8]).

| Composition       | Average number of particles ($n_{av}$) | Particles size ($d_{av}$), µm |
|-------------------|---------------------------------------|--------------------------------|
|                   | <1   | 1…2 | 2…4 | 4…6 | 6…10 | 10…20 | 20…30 |
| InP               | 7    | 41   | 36   | 36   | 12    | 11    | 5     |
| InP$_{0.18}$CdTe$_{0.82}$ | 19    | 62   | 20   | 28   | 16    | 3     | –     |
| InP$_{0.16}$CdTe$_{0.84}$ | 65    | 56   | 17   | 16   | 4     | –     | –     |
| InP$_{0.12}$CdTe$_{0.88}$ | 7     | 16   | 40   | 50   | 14    | 19    | –     |
| InP$_{0.09}$CdTe$_{0.91}$ | 11    | 42   | 30   | 38   | 16    | 8     | 2     |
| CdTe             | 8    | 68   | 26   | 18   | 16    | 11    | –     |

The correlation between the density values ($\rho_r$) obtained from X-ray patterns and the average number of particles ($n_{av}$) obtained from SEM images and ordinary microscopic images (Fig. 4) comes under notice.

If the relationship between $n_{av}$ and $\rho_r$ is logical, then the correlation between the results of $d_{av}$, $n_{av}$ determination from SEM images, obtained using the less expensive equipment is of some interest.
Figure 4. Dependence on the composition of the system InP-CdTe components of theoretical calculated crystal density – $\rho_r$ (1) and average number of the most displayed particles – $n_{av}$ (2) within the range of their size 4…6 µm

Taking into account the influence of $n_{av}$ on the coordinative unsaturation of the surface atoms responsible for Lewis acid sites, respectively, for the surface activity with respect to gases of a certain electronic nature, one can speak of a possible, easier estimation of the obtained materials suitability for manufacturing measuring cells using more available common microscopic images.

6. Conclusions
Using the improved isothermal diffusion method of the initial binary compounds (InP, CdTe), solid solutions (InP)$_x$(CdTe)$_{1-x}$, were obtained, certified according to X-ray, submicroscopical and microscopical studies as substitution solid solutions with sphalerite structure.

The consistent patterns were revealed in the studied bulk properties compositional changes: parameter value (a), crystal lattices interplanar distances (d$_{hkl}$), theoretical calculated crystal density ($\rho_r$), average size ($d_{av}$) and average number of the most displayed particles. The constitutional diagrams “property – composition” were plotted evidencing both statistical and extreme factors.

Based on the correlations between them and the correlations between $d_{av}$, $n_{av}$, revealed through applying various methods, a method of approximate, easier search for the advanced materials suitable for the manufacturing of the corresponding measuring cells was proposed.
7. References

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