

## Doping methods and properties of the solid solutions on $A^{II}B^{VI}$ crystals base

*L.V.Atroshchenko, L.P.Gal'chinetskii, S.N.Galkin, K.A.Katrunov, A.I.Lalayants, E.K.Lisetskaya, I.A.Rybalka, V.D.Ryzhikov, V.I.Silin, N.G.Starzhinskii, E.F.Voronkin*

Institute for Scintillation Materials, STC "Institute for Single Crystals",  
National Academy of Sciences of Ukraine, 60 Lenin Ave.,  
61001 Kharkiv, Ukraine

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It has been shown that the composition and concentration of complex radiative recombination centers in solid solution crystals in  $A^{II}B^{VI}$  systems depends along what section of the concentration triangle is the solid solution obtained. Effects have been studied of the isovalent dopant and thermal treatment in different media upon optico-luminescent, structural and physico-chemical characteristics of solid solution crystals in the ZnSe–ZnTe system.

Установлено, что состав и концентрация комплексных центров излучательной рекомбинации кристаллов твёрдых растворов (ТР) в системах  $A^{II}B^{VI}$  зависят от того, по какому разрезу концентрационного треугольника происходит образование ТР. Исследовано влияние изовалентной примеси и термообработки в различных средах на оптико-люминесцентные, структурные и физико-химические характеристики кристаллов ТР в системе ZnSe–ZnTe.

The interest in binary semiconductors with isovalent dopants is due to their functional properties [1, 2]. In particular, crystals of zinc selenide doped with tellurium (ZnSe(Te)), characterized by their unique electrophysical and scintillation parameters, are widely used for dosimetry of gamma- and X-ray radiation and as cathodoluminophores, being distinguished by their high radiation stability [3].

These parameters can be varied by growing crystals of solid solutions (SS) of  $A^{II}B^{VI}$  type compounds with specified composition. Examples of  $A^{II}B^{VI}$ -type SS widely used in many fields of science and technology are CdTe–ZnTe, CdS–CdTe, ZnSe–ZnTe. The best studied is the system ZnSe–ZnTe. Taking this system as an example, we will consider effects of various physico-chemical and technological factors upon composition, structure and different properties of  $A^{II}B^{VI}$ -type crystal SS. It should be stressed that

most of the obtained results are, to some extent, also valid for other SS of this type. The best known method of doping zinc selenide with tellurium is SS preparation along a section in the Zn–Se–Te system.

Thermodynamic analysis shows [4] that SS composition and structure in the ZnSe–ZnTe system are largely dependent upon what section of the Zn–Se–Te phase diagram is involved in the interaction of the components. The model [4] suggests that at low concentrations of tellurium ( $C_{Te} \ll 1\%$ ), when both isolated  $Te_{Se}$  atoms and complexes involving  $Te_{Se}$  can be considered as independent defects, the inequality  $U_1 > U_2 > U_3$  holds, where  $U_1$ ,  $U_2$ ,  $U_3$  are the formation energies of an isolated  $Te_{Se}$ , doublet  $V_{Zn}Te_{Se}$ , and triplet  $Zn_iV_{Zn}Te_{Se}$ , respectively. This inequality means that at small  $C_{Te}$  in the equilibrium state there are practically no isolated  $Te_{Se}$  atoms in this system. A simple estimate shows that only at  $C_{Te} < 10^{17} \text{ cm}^{-3}$

the distances between isolated  $\text{Te}_{\text{Se}}$  and between complexes involving  $\text{Te}_{\text{Se}}$  in ZnSe crystals exceed 30–40 interatomic distances; in this case, interaction between them can be neglected. This means that, at the Te doping level of the order of  $10^{20} \text{ cm}^{-3}$ , which corresponds to  $C_{\text{Te}}$  about 1 %, only 0.1 % of Te atoms are introduced into the ZnSe lattice in the form of  $\text{Te}_{\text{Se}}$ .

The model [5] suggests that doping of ZnSe crystals with tellurium and subsequent thermal treatment (TT) in zinc vapor gives rise to stable triple complexes  $\text{Zn}_i\text{V}_{\text{Zn}}\text{Te}_{\text{Se}}$  of low mobility, which are considered as radiative recombination centers (RRC-1) with  $\lambda_{\text{max}} \approx 635 \text{ nm}$ . Doping of ZnSe by isovalent oxygen ( $\text{O}_{\text{Se}}$ ) and TT in Zn vapor lead to formation of stable complexes  $\text{V}_{\text{Zn}}\text{Zn}_i\text{O}_{\text{Se}}$  (RRC-2 with  $\lambda_{\text{max}} \approx 605 \text{ nm}$ ). The reason for stability of these complexes is that isovalent substitution of tellurium for selenium, with Te having larger crystallochemical dimensions, the lattice is tending to expand, and local elastic stresses appear. If in the first coordination sphere  $\text{Te}_{\text{Se}}$  the vacancy is formed in the zinc sublattice, with smaller effective radius as compared with Zn atom, this leads to compensation of elastic stresses, i.e., to lowering of the internal energy of the system. Moreover, the electrostatic interaction between  $\text{V}_{\text{Zn}}$  (acceptor) and  $\text{Te}_{\text{Se}}$  (effective donor) also lowers the system energy. Addition of  $\text{Zn}_i$  to the stable doublet  $\text{V}_{\text{Zn}}\text{Te}_{\text{Se}}$  from the side of  $\text{V}_{\text{Zn}}$  leads to a further decrease in both elastic and Coulomb components of the internal energy of the system; therefore, the triplet  $\text{Zn}_i\text{V}_{\text{Zn}}\text{Te}_{\text{Se}}$  thermodynamically is even more stable. A similar mechanism can explain stability of complexes  $\text{V}_{\text{Zn}}\text{Zn}_i\text{O}_{\text{Se}}$ : the Coulomb interaction between donor  $\text{Zn}_i$  and effective acceptor  $\text{O}_{\text{Se}}$  and the need for compensation of local elastic stresses around  $\text{O}_{\text{Se}}$  make the formation of  $\text{V}_{\text{Zn}}\text{Zn}_i\text{O}_{\text{Se}}$  triplet energetically favorable. In this triplet,  $\text{Zn}_i$  is a direct neighbor of  $\text{O}_{\text{Se}}$ .

It follows from [4] that the structure of the complexes depends upon the direction of a section in the Zn–Se–Te system: in doping along the ZnSe–Te section, predominant are doublets  $\text{V}_{\text{Zn}}\text{Te}_{\text{Se}}$ , in doping along ZnSe–ZnTe, predominant are triplets  $\text{Zn}_i\text{V}_{\text{Zn}}\text{Te}_{\text{Se}}$ . It should be stressed again that such mechanism of SS formation along the said sections can be realized only in the region of low ( $C_{\text{Te}} \ll 1 \%$ ) concentrations of ZnTe or tellurium in ZnSe, when the complexes are independent. If concentrations of the binary

components are comparable, both elastic and electrostatic energy of Te in substitution positions is decreased, because both the average atomic radius and the average effective charge become closer to the corresponding parameters of ZnTe. Therefore, at sufficiently large ZnTe content, the formation of  $\text{Zn}_i\text{V}_{\text{Zn}}\text{Te}_{\text{Se}}$  complex with energy loss for formation of vacancies and interstitials is no longer favorable, and the solution mechanism crosses over to classical substitution.

The concentration of doublets  $C_2$  and triplets  $C_3$  is strongly dependent upon  $C_{\text{Te}}$ , tellurium concentration and deviations from stoichiometry (the initial vacancy concentration is  $C_{\text{V}}^0$ )

$$C_2 = \frac{1}{2D} \left[ D \cdot C_{\text{Te}} + D \cdot C_{\text{V}}^0 + 1 - \sqrt{(C_{\text{Te}} - C_{\text{V}}^0)^2 + D^2 + 2D(C_{\text{Te}} - C_{\text{V}}^0) + 1} \right] \quad (1)$$

$$C_3 = C_{\text{Te}} - C_2. \quad (2)$$

Here

$$D = \frac{\alpha_2}{\alpha_3} \exp\left(\frac{-(U_2 - U_{\text{V}}) - U_3}{kT} - \frac{\sigma_3 - \sigma_2}{k}\right),$$

where  $\alpha_2$  and  $\alpha_3$  are statistical weights of doublets and triplets, while  $\sigma_2$  and  $\sigma_3$  is the entropy of lattice deformations in the vicinity of each of them.

From (1), (2) it is clear that with increasing  $C_{\text{Te}}$  concentrations of both doublets and triplets are increasing practically linearly, with the doublet predominance also increasing (e.g., at  $|U_2 - U_{\text{V}}| = 0.5 \text{ eV}$  and  $U_3 = 0.1 \text{ eV}$  — by two times, at  $|U_2 - U_{\text{V}}| = 0.5 \text{ eV}$  and  $U_3 = 1 \text{ eV}$  — by three orders). This is in agreement with the initial statement that doublet formation is energetically favorable with already present  $C_{\text{V}}^0$ . With higher  $C_{\text{V}}^0$   $C_2$  increases at the cost of decreasing  $C_3$ .

In the case when there are no deviations from stoichiometry, and the doping affects stoichiometrical ZnSe ( $C_{\text{V}}^0 = 0$ ), the equation (1) can be transformed as:

$$C_2 = C_3 \cdot H \cdot \exp(2[C_{\text{Te}} - C_3]), \quad (3)$$

where

$$H = \frac{\alpha_2}{\alpha_3} \exp\left(-\frac{(U_3 - U_2)}{kT} - \frac{\sigma_3 - \sigma_2}{k}\right).$$

Numerical solution of (3) under assumption that  $U_2 - U_3$  is varied from 0.1 eV to

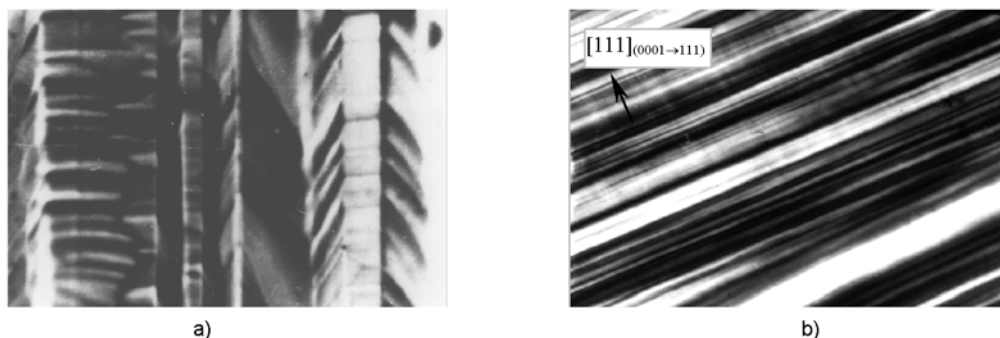


Fig. 1. Thermal etching bands on the outer side (a) and birefringence bands on plane (110), normal to plane  $(111)_{(0001 \rightarrow 111)}$  (b) of crystals ZnSe and ZnSe(Te) at  $C_{Te} < 0.3\%$  in polarized light. The crystals have packing defects of twinning type. Magnification  $44\times$ .

1 eV gives the following result: the concentration of triplets substantially exceeds that of doublets (at  $U_2 - U_3 = 0.1$  eV, the surplus is by one order, at  $U_2 - U_3 = 1$  eV – by four orders). In other words, in stoichiometric ZnSe the predominance of triplets strengthens with increasing  $C_{Te}$ . Thus, taking into account that just the triplets are responsible for emission in ZnSe( $Te_{Se}$ ,  $O_{Se}$ ) crystals, it is clear that preparation technology of such SS should ensure minimum deviations from stoichiometry.

The luminescence intensity, its spectrum and kinetics in ZnSe( $Te_{Se}$ ) and ZnSe( $O_{Se}$ ) crystals are determined, primarily, by the above-noted RRC-1 and RRC-2. In real crystals, depending upon peculiar features of their preparation technology, all these types of defects can be present in larger or smaller quantities. The SS composition, as well as ways of its variation (e.g., using TT in different media), can substantially affect not only optico-luminescent characteristics of ZnSe( $Te_{Se}$ ,  $O_{Se}$ ) crystals, but also their structure and physico-mechanical properties, which is the main subject of our further considerations.

The samples for studies were cut from crystals ZnSe( $Te_{Se}$ ) (crystals K1), ZnSe( $O_{Se}$ ) (crystals K2), grown by the Bridgman method in vertical compression furnaces in argon atmosphere at the pressure up to  $5 \cdot 10^6$  Pa. Special attention was paid to mechanical treatment of the crystals, since mechanical properties of different  $A^{II}B^{VI}$  type compounds had been known to be very different. E.g., the structure of Bridgman-grown ZnSe(Te) crystals is of large blocks with twinning layers due to uncompleted wurtzite-sphalerite phase transition. High tendency of these crystals to cracking is due both to these factors and to the residual thermoelastic stresses. Moreover, under me-

chanical treatment the depth of the disturbed layer can be different for different samples, reaching the values of several tens of microns, which can naturally affect the results obtained in studies of structural parameters. The samples were cut from crystals by diamond discs. Then they were fixed by an adhesive and treated with corundum grinding powders of different grain size, thus obtaining the required size. The grinded-out layer depth was up to several hundreds of microns, which allowed the removal of residual cleavages and fissures occurred in cutting, minimizing at the same time the depth of the disturbed layer.

Some of the K1 and K2 samples, including those subject to thermal treatment (TT) in Zn or Te vapor, were thermally treated under hydrogen flow at  $T \approx 1200$  K for 3 hours. The concentration of activator dopants was controlled using X-ray fluorescence analysis. The microstructure defects were studied by an optical microscope using polarized light and phase contrast techniques. Studies of brittle destruction of ZnSe $_{1-x}$ Te $_x$  crystals was carried out by micropressing with an indenter using a PMT-3 instrument. X-ray luminescence (XL) spectra were studied using a KSVU-23 complex; a REIS device was used as a source of exciting radiation. The optical transmission of ZnSe samples close to the fundamental absorption edge (in the 450–600 nm) was measured by a KSVU-23 complex. All measurements were carried out at  $T = 300$  K.

It is known [1] that ZnSe-based crystals can crystallize either in the wurtzite (W) or sphalerite (S) structure, depending on specific conditions of their preparation. Both W and S structures are characterized by tetrahedral coordination of atoms and differ in the filling sequence of densely packed layers (0001) in W and (111) in S. Viola-

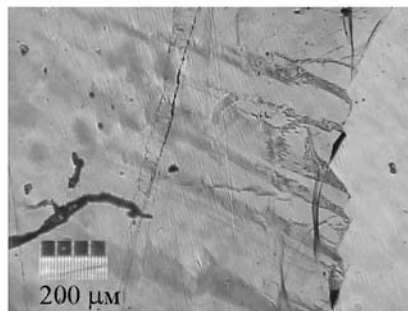
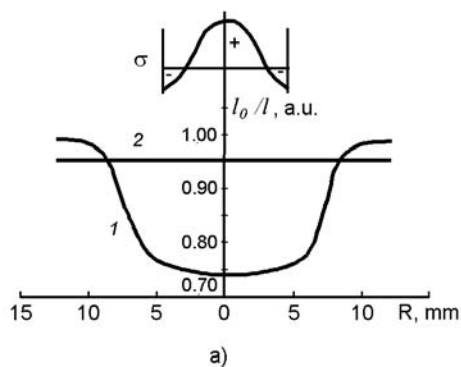


Fig. 2. (a) Distribution of the relative brittle strength of ZnSe(Te) crystals along the radial cross-section: 1 — after growth, 2 — after thermal treatment (Insert: distribution of residual thermal stresses). (b) Network of microfissures in the central part of ZnSe(Te) crystals after growth.

tions of these sequences gives rise to packing defects, which can be described as alternating wurtzite and sphalerite phase regions. Incompleteness of the  $W \rightarrow S$  phase transition leads also to formation of polytypes and twinning. Outer signs of the presence of packing defects related to the phase transition incompleteness in ZnSe crystals are characteristic inclined bands on the surface of the grown crystals, which can be observed visually (Fig. 1a). The bands can have width from 1 micron to several millimeters, which is related to different orientation of light-reflecting surfaces (110) and microcavities due to thermal etching occurring during cooling of the crystal.

In polarized light, birefringence bands are observed on planes (110) of ZnSe crystals. The birefringence in these crystals is directly related to mechanical stresses emerging in polysynthetic twinning during the phase transition. Microscopic studies of ZnSe(Te) crystals with Te concentration from 0.01 to 0.7 % in polarized light has shown that at  $C_{Te} < 0.3$  % they are also characterized by birefringence as the undoped ZnSe (Fig. 1b), which is not observed at  $C_{Te} > 0.3$  %. This means that packing defects are not formed in ZnSe at  $C_{Te} \geq 0.3$  %. In other words, doping of ZnSe with tellurium at  $C_{Te} \geq 0.3$  % stabilizes the sphalerite structure. The presence of packing defects creates layer-like non-uniformity of the material, which leads to anisotropy of optical and mechanical properties. Studies of mechanical properties has shown that in the central part of the crystal the microhardness value  $H_{\mu}$  is by ~14 %, and the value of brittle strength  $\sigma_{str}$  — by ~22 % lower as compared with the peripheral part. Fig. 2a shows relative changes in

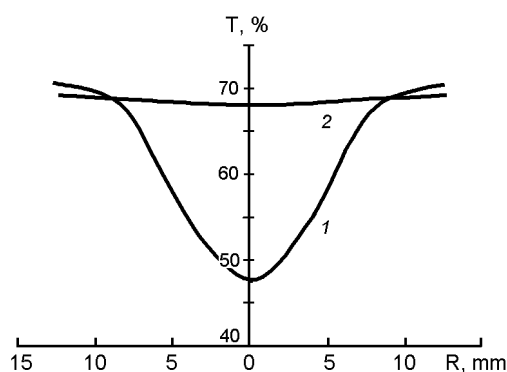


Fig. 3. Distribution of optical transmission of  $ZnSe_{1-x}Te_x$  crystals along the radial cross-section: 1 — after growth, 2 — after thermal treatment.

the fissure length around the indenter imprint ( $l_0/l$ , where  $l_0$  is the fissure length in the peripheral part of the crystal) over the cross-section of a ZnSe(Te) crystalline ingot, which characterizes the relative brittle strength of the material.

Such scatter in  $H_{\mu}$  and  $\sigma_{str}$  values is explained by the presence of stretching and compressing tensions in the crystal after growth. Stretching tensions in the central part of the crystal lead to formation of a developed network of microfissures (Fig. 2b), which favors substantial worsening of the mechanical strength. It is important to note that TT of crystals leads to substantial microstructural changes: microfissures in the central part of the crystal disappear. The value of brittle strength is increased (Fig. 2a, curve 2), and uniformity of this value is observed over the radial cross-section. Thus, the level of residual internal stresses is lowered. In Fig. 3, (curve 1), one can see a typical plot for optical transmission of the crystal after growth. The tran-

spareness in the central part of the ingot is 30 % lower than near the edges. One of the reasons of worse optical transmission in the center is the presence of residual internal stresses in ZnSe(Te) crystals. One should account for one more important factor that adversely affects the optical transmission. As noted above, at the Te doping level of ~1 % (which corresponds to  $C_{Te}$  of about  $10^{20} \text{ cm}^{-3}$ ) only 0.1 % of Te atoms enter the ZnSe lattice in the form of  $Te_{Se}$ . Hence it can be concluded that the bulk fraction of the introduced tellurium is a part of the metastable  $SS \text{ ZnSe}_{1-x}\text{Te}_x$ , and is also accumulated at dislocations. In addition, the electron microscopy data also suggest that some of Te atoms are forming clusters. All this can result in additional scattering and absorption centers. After annealing in Zn vapor, the optical transmission in the central part of the crystal is increased and becomes distributed practically uniformly over the cross-section (Fig. 3, curve 2). This is an evidence that the whole crystal becomes more structurally perfect after TT.

In [6], it was established that isovalent doping with Te at concentration of ~0.6 % and TT in Zn vapor lead to a substantial increase in polarizability of ZnSe crystals and, consequently, to unusually high values of dielectric permittivity (by 1–2 orders). This additionally confirms that, as a result of isovalent doping, electrically active complexes are formed in the crystals, which are distinguished by their high dipole moment.

TT in Zn vapor of  $\text{ZnSe}(\text{Te}_{Se})$  crystals (samples K1) and  $\text{ZnSe}(\text{O}_{Se})$  crystals (samples K2) increases by tens of times the concentration of complexes  $V_{Zn}Zn_iO_{Se}$  and  $Zn_iV_{Zn}Te_{Se}$  — up to  $10^{17} \text{ cm}^{-3}$ , and the structural perfection is improved correspondingly [7]. However, TT of samples K1 and K2 in hydrogen leads to substantially different results, which suggests that the character of interaction is different. This character becomes clear if we analyze XL spectra in the region of intrinsic emission. It can be seen from Fig. 4 that TT in hydrogen of the K1 sample that had been pre-annealed in Zn vapor leads to slight changes in XL intensity (IXL) and does not affect at all the position of  $\lambda_{max}$ , (the same value of ~635 nm that is characteristic for RRC-1). This implies that  $Zn_iV_{Zn}Te_{Se}$  complex is inert with respect to hydrogen. However, TT in hydrogen of K2 (also pre-annealed in Zn vapor) causes IXL to decrease by several times, and  $\lambda_{max}$  is substantially shifted to longer wavelengths: from 605 to 630 nm. The

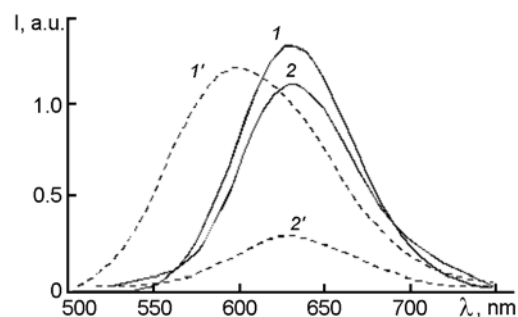


Fig. 4. X-ray luminescence spectra of samples K1 (1, 2) and K2 (1', 2') subject to preliminary thermal treatment in Zn vapor: 1, 1' — without thermal treatment in hydrogen; 2, 2' — after subsequent thermal treatment in hydrogen.

concentration of free carriers, evaluated from IR absorption measurements, is decreased by more than an order after TT in hydrogen of K2. Keeping in mind that RRC-2 has  $\lambda_{max} \approx 605$  nm, and  $\lambda_{max} \approx 630$  nm is related to radiative recombination of the pair  $Zn_iV_{Zn}$  [8], the data of Fig. 4, as well as estimates of the free carrier concentration, lead to conclusion that hydrogen does actively interact with the  $V_{Zn}Zn_iO_{Se}$  complex, binding its oxygen and moving it away from the complex. The result of such interaction is the transformation of the complex into a closely bound pair or its decomposition under the scheme  $H_2 + V_{Zn}Zn_iO_{Se} \rightarrow Zn_{Zn} + H_2O \uparrow$ . This assumption is further confirmed by the fact that subsequent TT in Zn vapor does not lead to any noticeable changes in IXL and  $\lambda_{max}$ .

In conclusions, taking as examples solid solutions of the system ZnSe–ZnTe, we have established that composition and concentration of radiative recombination centers, which determine optical and luminescent characteristics of the crystal, are dependent upon the section of the ternary system Zn–Se–Te along which the solid solution is formed. The RRC concentration is low, involving only a small fraction of the isovalent dopant atoms in the solid solution. Structural, physico-chemical and mechanical characteristics of the solid solution crystals are determined by the overall content of isovalent dopant atoms in the solid solution. Mechanisms have been studied of the effects of thermal treatment in different media upon characteristics of the solid solution crystals.

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## Способи легування та властивості твердих розчинів на основі сполук $A^{II}B^{VI}$

**Л.В.Атрощенко, Л.П.Гальчинецький, С.М.Галкін,  
К.О.Катрунов, О.І.Лалаянц, О.К.Лисецька, І.А.Рибалка,  
В.Д.Рижиков, В.І.Сілін, М.Г.Старжинський, Є.Ф.Воронкін**

Встановлено, що склад і концентрація комплексних центрів випромінювальної рекомбінації кристалів твердих розчинів (ТР) у системах  $A^{II}B^{VI}$  залежать від того, вздовж якого розрізу концентраційного трикутника відбувається утворення ТР. Досліджено вплив ізовалентної домішки і також термообробки у різних середовищах на оптико-люмінесцентні, структурні й фізико-хімічні характеристики кристалів ТР у системі ZnSe–ZnTe.