# Luminescent properties of ZnS single crystal annealed in the V<sup>th</sup> group elements melt

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The influence of ZnS single crystal annealing in the media based on V-group elements Bi and Sb on its photoluminescent (PL) properties was studied. The following media: Bi, Sb, Bi+Zn, Sb+Zn, Bi+S, Sb+As and Bi+Al were used for the annealing. Two types of the starting crystals were used: I) low resistivity ZnS; II) high resistivity ZnS. The annealing was carried out in the vacuumed silica ampoules at the temperatures of 1400 K (I) and 1200 K (II) during 100hrs. The obtained results show that ZnS crystals annealing in Bi and Sb melts leads to the analogical reorganization of radiation centers based on the native and impurity defects generated by interphase interaction at ZnS-melt interface. These defects are responsible for the appearance of the green radiation having the feature of intracentred transitions. The high value of green band half-width indicates that it is a superposition of a few bands. These could be a PL bands related to the oxygen presence, the impurity centers of the V group elements and to $V_S$.

## 1. Introduction

Zinc sulfide a wide gap II-VI semiconductor is rather widely used due to its unique properties. ZnS single crystals are used in the fabrication of diodes. Its powders are used mainly as a phosphor. ZnS properties, very sensitive to native defects and impurities are a subject of numerous studies.

One of the possible ways in the creation and control of the radiation centers set based on native and impurity defects is the crystal annealing in different metal melts. The dissolved in the melt impurity directly interacts with the solid state lattice. The impurity diffusion occurs in the steady conditions determined by the interaction at the crystal-melt interface. Therefore the quest for proper media for defects set control in the crystal is a rather topical problem. From this point of view, a promising medium for the annealing in the melt and doping by the impurity from the melt, the V group elements such as Bi and Sb could be. These elements have a rather low melting temperature (271 $^\circ$C for Bi and 631 $^\circ$C) and a relatively low value of saturated vapors pressure. The tetrahedrical radius value for Sb (1,36 Å) and for Bi (1,46 Å) is higher than for Zn (1,25 Å) and S (1,04 Å) which allows supposing that their inculcation into ZnS lattice during the annealing is complicate. This supposition was confirmed by the results brought in the paper [1] at the investigation of ZnSe crystals annealed in Bi melts, where the crystal cleanup of a series of uncontrolled impurities was observed and no luminescence bands that could be related to Bi impurity were observed. In spite of the perspectiveness of V group elements using as an annealing and doping medium for zinc sulfide crystals, the problem of the nature of the radiation centers influenced by the V

group elements during the annealing or includes them as a component still remains unclear.

The objective of this work consists in the investigation of the influence of ZnS annealing in the Bi and Sb based on its luminescent properties of zinc sulfide, studies of the possibility of Bi and Sb atoms building into) the ZnS lattice, and of the native defects and oxygen role in these processes.

## 2. Experimental

The main native defects in zinc sulfide are sulfur vacancies $V_S$, zinc vacancies and inter knots zinc $Zn_i$. The main native defect stipulating the ZnS n-type conductivity is $V_S^+$. At the fabrication of high conductivity zinc sulfide the Al impurity is often used which being build into the zinc knots creates $Al_{Zn}^+$ defects and also creates $(V_{Zn}^{--} Al_{Zn}^+)^-$ and $Al_{Zn}^+-(V_{Zn}^{--}Al_{Zn}^+)^-$ centers [2].

Bi and Sb manifest the valence +3 and -3. Therefore as the build into the zinc knots of ZnS lattice they will create donor centers and the build into sulfur knots – the acceptor ones. In some cases the V group impurity in II-VI compounds could simultaneously inculcate both in the anion ones [3], i.e. is an amphoteric impurity.

Two types of zinc sulfide bulk crystals annealed in the Bi and Sb based melt were the subject of the investigations in this paper: low ohmic (type I) and high ohmic (type II). As an annealing media the bismuth and stibium melts containing Bi+1,3at% of Zn, Sb+12at.% of Zn, Bi+1 at.% of S, Sb+0,01 at% of $As_2S_3$, Bi+0.01at.% of Al were used.

The annealing was carried out in the sealed silica ampoules at the temperature of 1400 K for the crystals of type I and 1200 K for the crystals of type II. The annealing

duration was 100 hours. The melt volume exceeded the crystal volume by 10 times. After the termination of the annealing the ampoule was cooled in the air. Then the crystals were cleaved perpendicular to the surface contacting the melt.

The PL studies on freshly cleaved surfaces were carried out at 77 K and 300 K in the wavelength region of 340…700 nm. The PL excitation was carried out by a nitrogen pulse laser $\tau$=10 ns, $\lambda_{exc}$=337 nm (3.68 eV). The PL signal recording was carried out by synchronized detecting method on a unit based on MDR-2 monocromator and FAU-79 photomultiplier.

By taking into account that previously obtained date [4,5] about the radiative centers set near the enriched with the dislocations surface contacting with the melt and in the crystal volume, the measurements were carried out at the excitation of different crystal regions by a focused laser beam near surface (surface) and in the bulk of the crystal (volume). The diameter of excitation aria was ~1 mm.

## 3. Results

In the PL spectrum at 77 K of the I type crystal the violet band with the maximum at 390…400 nm predominates (Fig. 1, curve 1), which is apparently a superposition of at least two bands stipulated by the $V_S$ and $Al_{Zn}$ based centers with the maxima situated at 405 nm and 380 nm [6]. The annealing in Bi (surface) and Sb (Fig. 1, curves 2, 3, 4) shifts the violet band maximum to the long wavelength region at 400…410 nm. Its relative intensity decreases. As it was mentioned, the luminescence in this region of spectrum is related to $V_S$. According to our studies [7], at ZnS:Al annealing in Bi melt (as well in Sb) the Al extraction from the crystal occurs. The contribution in PL of Al based radiation centers decreases and the violet band shifts to 410 nm. At the same time the destruction of $V_{Zn}^{-}Al_{Zn}^{+}$ associates occurs. This leads to the increase of zinc vacancies concentration and as a result to the increase of the luminescence intensity at 440…450 nm caused by the $V_{Zn}$ centers (Fig. 1, curves 3, 4, 5). Another $V_{Zn}$ source is zinc vacancies generation due to partial zinc dissolving from the crystal. The sulfur transition from the crystal to the melt is difficult at the used treatment medium and temperatures. The same change in PL spectrum in the region of 440…450 nm is observed at the crystal annealing in vacuum. One know that the annealing in vacuum is the same as annealing in sulfur vapors [6] due to higher volatility of sulfur comparable with zinc in ZnS. $V_{Zn}$ are also generated during this process.

After the annealing in Zn and Sb melt in the PL spectrum the violet band position does not change comparable with the starting crystal (Fig. 1, curve 5). This fact, obviously, confirms the assumption about the zinc extraction from the crystal during the annealing in Bi and Sb; so the zinc addition into the melt the correlation between Zn, $V_{Zn}$ and $Al_{Zn}$ changes less than in the zinc absence. One can assume that the added zinc amount was

not enough for to avoid zinc dissolving in the melt at the annealing temperature.

As a result of ZnS annealing in Bi (surface) and Sb, Sb+Zn and in vacuum in the green region of PL spectrum an intensive radiation with the maximum in the range of 530…550 nm appears (Fig. 1, curves 3, 4, 5). The relative intensity of this luminescent radiation has the highest value after the annealing in Sb and Sb+Zn. The band half width is higher than 300 meV. Obviously this band is a superposition of a few bands caused, for example, by Bi(Sb) [8], $V_S^{2+}$[6] and oxygen [2]. The oxygen spreads in the crystal at the annealing in Sb and Bi at 1400 K is not excluded. In [8] this radiation was related to the intracentered transitions of Bi based centers. One can assume that Sb and Bi form analogous centers in ZnS.
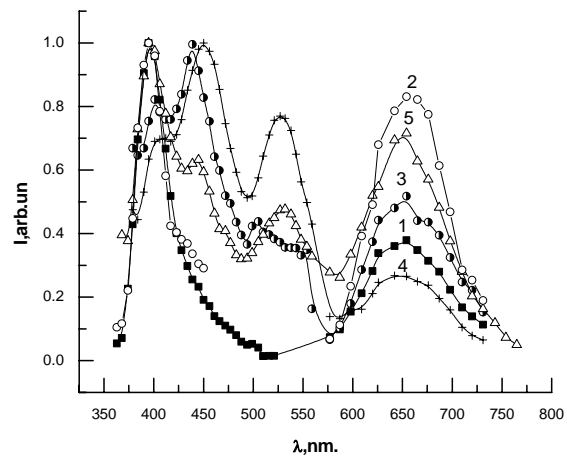


*Fig. 1. PL spectra of ZnS crystals (I) at 77 K. 1-starting crystal; 2- annealed in Bi melt (volume); 3- annealed in Bi melt (surface); 4- annealed in Sb melt; 5- annealed in Sb+Zn melt.*

A considerable contribution of a radiation with the energy of 1.80…1.91 eV (650…670 nm) which does not depend on annealing condition and corresponds to the centers situated close to the ZnS band gap middle ($E_{g77K}$=3.82 eV) in ZnS PL indicates apparently to the dislocation nature of these centers. This band was also observed in the PL spectrum of the starting crystals of type II.

In the experiments with the starting crystals of type II almost the same regularities were observed as for the type I crystals. The difference between PL spectra at 77 K of these samples with the above described, obviously, is caused by the possible Al doping of the I type crystal. The annealing temperature in this case did not exceed 1200 K.

For the samples annealed in the Bi melt the same spectrum structure as in the starting sample with the predominant maximum at 395 nm (for the starting sample – 390 nm) and the red radiation with the maximum at 650…670 nm was observed. At the level of 90% for the PL maximum intensity a peculiarity appears at 400…405 nm. The PL integral intensity decreases by ten

times comparable to the starting sample. The radiation in the region of 450…460 nm, caused by $V_{Zn}$ and $Al_{Zn}$ is poorly pronounced. The green luminescence is not observed. The ZnS annealing in $Bi+S_2$ (Fig. 2, curve 1) leads to the shift of the PL "violet" principal maximum to the short wavelength region and its position coincides with that of the starting sample. At the addition of 1,3 at.% of Zn in the Bi melt in the PL spectrum of ZnS crystals (Fig. 2, curve 2) a shift of the violet band at 400 nm is observed. The red band position does not change Unlike to the annealing in Bi the PL maximum close to 580…590 nm appears which is related to $Mn_{Zn}^{2+}$ based centers [9]. One can assume that both Bi as well as S presence in the melt generate zinc vacancies in ZnS and the manganese which according REP investigations is contained in ZnS(ZnSe) occupies the zinc knots and stipulates the appearance of $Mn_{Zn}^{2+}$ centers radiation. The $V_{Zn}$ centers based radiation (in the region of 440-450 nm) could be the resonance excitation radiation for $Mn_{Zn}^{2+}$ centers. Some other explanations of manganese radiation appearance are possible. We can ascertain only that for the observation of this radiation at 77 K the sulfur presence in the Bi melt is necessary. At 300 K the manganese band appears in the II type crystal spectrum at their annealing only in Bi. So as the excitation source at 300 K it works the radiation, which is absent in the above described sample. The "green" band with the maximum close to 540 nm in PL spectrum at 77 K was observed for the samples annealed in Bi melt with the addition of a certain amount of Al (Fig. 2, curve 4).
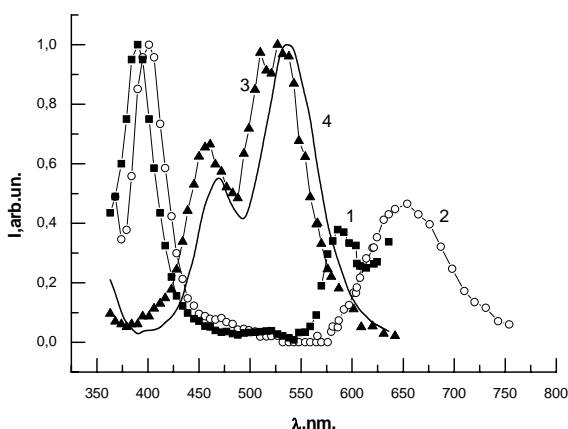


*Fig. 2. PL spectra of ZnS crystals (II) at 77 K. 1-annealed in Bi+S; 2-annealed in Bi+Zn; 3-annealed in Sb+As$_2$S$_3$; 4- annealed in Bi+Al.*

The most significant changes in the PL spectra at the addition in the Sb melt of $As_2S_3$ (Fig. 2, curve 3) and at Al addition in Bi melt occur (Fig. 2, curve 4). The PL spectrum of these samples consists of two bands: the first of it with the maximum at 460 nm and the second with two maxima at 510 nm and 530 nm. At 300 K the PL spectrum of this sample is represented by a single band with the maximum at 530 nm. One should mention that the green

band (530…540 nm) appears in PL spectrum of ZnS crystals after their annealing in Sb based melts if Al impurity is present in the starting crystal (Fig. 1, curves 4, 5) or if it is added in Bi melt (Fig. 2, curve 4).

In the PL spectra at 300 K of the samples type I starting crystals the green radiation with the maxima in the region of 530…540 nm is observed after almost all carried out annealing (Fig. 3, curves 2…5). The narrowest green band with the maximum at 530 nm was revealed in PL spectra of the samples annealed in Sb and Sb+Zn (Fig. 3, curves 4, 5). After the annealing in Bi (Fig. 2, curves 2,3) both in the bulk volume and near surface contacting with the melt during annealing the PL band becomes much larger, and the peculiarity in the region of 460-470 nm coincides with the PL maximum revealed in the starting ZnS:Al at 300 K (Fig. 2, curve 1) and could be related to the $Al_{Zn}$ and $V_{Zn}$ based centers. Bat the PL distribution is not homogeneous on the crystal thickness of 2…3 nm. The homogeneous radiation was obtained for the sample thinner than 0.3 mm.

A distinctive feature of the studied samples annealed in Bi and Sb based melts is the appearance of a green luminescent band with the maximum of 530…540 nm in their PL spectrum. One's attention could be drawn by the green band behavior at 77 K and 300 K. For the samples annealed in Bi (surface)(I), Sb(I), (Sb+Zn)(I), (Sb+As)(II) and (Bi+Al)(II) this band is observed both at 77 K and at 300 K as well. At 300 K in the PL spectrum of these samples only a single one green band remains.

The obtained results show that ZnS crystals annealing in Bi and Sb melts leads to the reorganization of the radiation centers based on the native defects and impurities generated by the ZnS-melt interphase interaction. The appearance of the green PL band with the maximum at 530…540 nm is specific for the samples annealed in Bi and Sb melts. A characteristic feature of this band is preservation of the position of the maximum at the measurement temperature change from 77 K to 300 K (in the case of the annealing in Bi+Cl [8] the maximum position remains unchanged in the temperature range from 77 K to 410 K).
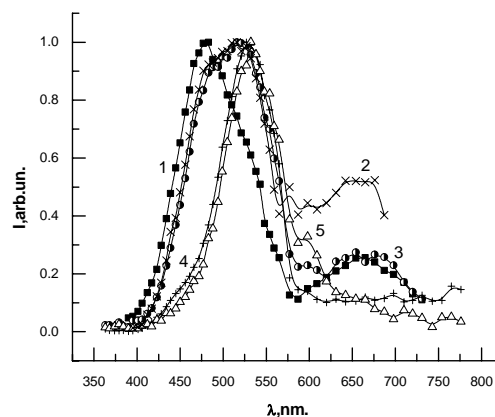


*Fig. 3. PL spectra of ZnS crystals (I) at 300 K. 1-starting crystal; 2- annealed in Bi melt (volume); 3- annealed in Bi melt (surface); 4- annealed in Sb melt; 5- annealed in Sb+Zn melt.*

Specific condition is necessary for the appearance of this band. This condition is the presence of Cl or Al, which are donor impurities for ZnS, either in the Bi melt or in the starting crystals or in both. In the absence of Cl or Al the green band is poor pronounced or misses at all. At the annealing in the vapors and melts at 1400 K a contribution of the oxygen in PL (radiation at 500…520 nm) is possible [2]. The homogeneous radiation was obtained for the sample thinner than 0.3 nm. The green band is observed at the heat treatment of ZnS in Sb at the addition of zinc in the melt (Fig. 1, 3, curves 4,5). The high value of this band half width shows that this is a superposition of a few bands. These can be the PL band caused by the oxygen presence (maximum at 500… 520 nm) and the radiation caused by the intracentered transitions of the V group element impurities (maximum at 530…540 nm) and of $V_S^{2+}$ (527 nm).The appearance of the last is stipulated by the zinc vacancies generation at the ZnS annealing in Bi and Sb media as well as by the possible inculcation of these elements atom in the knots of sulfur sub lattice, which leads to the change of the $V_S$ electric charge. One can assume that due to the processes occurring during annealing the formation of complex centers based on Bi and Sb such as $(Al_{Zn}^+Bi_S^-)$, $(Sb_{Zn}^+Sb_S^-)$, $(V_{Zn}^-Bi_{Zn}^+)^-$ and DX_centers in zinc sulfide is possible [7,9]. Then the obtained data confirm the amphoteric character of stibium in II –VI [3].

## 4. Conclusion

One can suppose that bismuth and stibium form or stipulate formation of similar defects in ZnS lattice. These defects are responsible for the green band radiation related to intracentered transitions in Bi and Sb based complex centers. Obviously, the stibium diffusion coefficient is higher than for Bi due to lower atomic radius, so that the doping with Sb atoms is more efficient.

The difference in PL spectra measured at the crystal surface and volume can witness that the depth of V group elements penetration depends on annealing temperature and the diffusion coefficient value is low. During the annealing the impurity has no enough time to diffuse at a whole crystal depth. The annealing in the V – group elements melt leads to the zinc sulfide cleanup of aluminum impurity and zinc extraction from the crystal to the melt.

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