

# Luminescence of Single Crystals of Manganese-doped Zinc Indium Binary Sulfides

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**Abstract** — Radiative recombination spectra of Mn-doped zinc tin indium single crystals have been analyzed in the work. The emission spectra interval close to its maximum (1,91±0,2) eV contains a number of the special features which were identified by us as intra-center transitions. We attribute the special features observed on the complex emission spectra to this type of transition by their decomposition into simple lines, using Alentsev – Foch method.

**Index Terms** —  $Zn_xIn_2S_{3+x}$  single crystals doped with manganese, spectra, gap width.

## I. INTRODUCTION

The advanced development of modern microelectronics and optoelectronics puts forward stringent requirements for the materials used. Current engineering and prospects of its further development require new technologies to prepare and study the physical properties of materials with unusual multifunctional properties. Depending on the devices for which the surface-barrier structures are used, they must have different characteristics, i.e., different dark resistivity, spectral regions of photosensitivity, and other parameters. It was shown in [1-4] that it is necessary to use relatively low-resistivity crystals to prepare UV sensors and high-resistivity layers for transmitting television tubes.

A particular role in the improvement of physical properties is played by the problem of doping materials and change in the energy spectrum of charge carriers induced by the dopants. In terms of both theory and practice, it is relevant to study the behavior of transition elements introduced in semiconductor crystals in different concentrations. This problem has been extensively studied

for compounds of the  $A^{II}B^{VI}$  and  $A^{III}B^V$  groups [5]. Therefore, scientific interest in complex semiconductor compounds has become more intense. Among promising

semiconductors, there are  $A^{II}B^{VI} - B_2^{III}C_3^{VI}$  compounds, including those of the  $A^{II}B_2^{III}C_4^{VI}$  group. In this family of semiconductor materials,  $Zn_xIn_2S_{3+x}$  ( $x=1÷5$ ) layered crystals stand apart. In terms of technology, the layered structure, the specificity of chemical bonds, and self-purification of tetrahedral packets make it possible to use them as the basis to prepare layered structures with planar parallel surfaces of different sizes, including those related to nanostructures.

Effective techniques for preparing these plate-like structures are described [3]. Despite the fact that the layered crystal structures of  $Zn_xIn_2S_{3+x}$  plate-like compounds (with strong covalent bonds in the layers and weak van der Waals bonds between the layers) have some

advantages over other semiconductor materials, they have not been applied enough. This situation is due to a number of yet unsolved problems. One of them is that these crystals, in common with other layered materials, are usually obtained in several polytypic modifications. Another difficult problem arises in connection with the study of changes in physical properties of layered structures under the influence of various ligands as well as control of the structure of intrinsic defects. In these materials the intercalation of the impurity between the layers can occur along with the traditional substitutional doping. Owing to this, the change in the characteristics of the material is more pronounced, because the impurities intercalated between the layers can lead to changes not only in the characteristics of charge carriers, but also in the nature of the impurity levels and to radical changes in the fundamental properties of the material. These materials are also very sensitive to modes of excitation of nonequilibrium charge carriers. The above problems determine the relevance of the study of the physical properties of  $ZnIn_2S_4$ (III) single crystals doped with manganese in different concentrations. Experimental data on the behavior of manganese in  $ZnS:Mn^{+2}$ ,  $ZnMnS$ ,  $ZnS:Mn^{+2}$ ,  $CdMnS$ , and other compounds have already been reported [6]. There are few published data on the effect of transition elements on the change in the energy spectrum of charge carriers in ternary compounds, such as  $Zn_xIn_2S_{3+x}$  and other compounds.

Mechanisms of the charge carrier recombination in manganese doped  $ZnIn_2S_4$  single crystals having different Mn-concentrations and their modification under the action of two different forms of excitation - electronic or photonic ones, were analyzed in this work. Radiation spectra were investigated depending on the temperature, manganese concentration and excitation process.

## II. EXPERIMENTAL RESULTS AND THEIR EXAMINATION

Radiative recombination spectra of  $ZnIn_2S_4:Mn$  single crystals with different concentration of manganese were obtained using standard procedures at 80K and 300K. The samples under the investigation were grown in

the closed volume from the vapor phase by the method of the chemical transport reactions, elementary components were undertaken in the stoichiometric proportion. The growth technology is described in the work [3].

This method makes it possible to combine for the reactions of synthesis and growth with the simultaneous doping with manganese in the single technological cycle. The samples under the investigation exhibit perfect single crystals with the thickness of  $(250 \div 300) \mu$  and the area of about one square centimeter. Manganese concentration in the investigated models was varied in the limits of  $(5 \cdot 10^{18} \div 2,5 \cdot 10^{20}) \text{ cm}^{-3}$ . The samples under investigation had n-type conductivity, which was determined on the basis of the analysis of galvanomagnetic effects.

For the samples being investigated, the absorption spectra at the temperatures of 80K and 300K were preliminarily taken. The width of the gap was determined in conformity with the absorption spectra form using a standard procedure. These experiments made it possible to obtain the following data for the width of the gap of the compounds being investigated:

$$E_g(300\text{K}) = (2,8 \pm 0,05) \text{ eV}$$

$$E_g(80\text{K}) = (2,95 \pm 0,05) \text{ eV}$$

The spectra of the radiative recombination of the doped compounds were taken from the plates with the area of  $0,3 \text{ cm}^2$  and thickness of  $(200 \div 300) \mu$  by means of two methods of excitation: under electron beam with the energy 60 keV and the current density  $10^{-2} \text{ A cm}^{-2}$  and photon - with the energy of the excitation quanta (laser)  $3,67 \text{ eV}$  ( $\lambda = 337 \text{ nm}$ ). The photoluminescent and cathodoluminescent spectra were obtained at two temperatures. To reveal the specific character of the process of excitation, the experimental dependences of an integrated intensity on the method and excitation level were investigated.

The results of the samples with manganese concentrations: 1 – [Mn]  $6,2 \cdot 10^{19} \text{ cm}^{-3}$ ; 2 – [Mn]  $1,9 \cdot 10^{20} \text{ cm}^{-3}$  at the temperature of 80K are presented in figures 1a and 1b.

a Fig. 1a presents  $I_{pl} = f(E)$  dependence in the case of the photon excitation, 1b – the results of the electronic excitation.

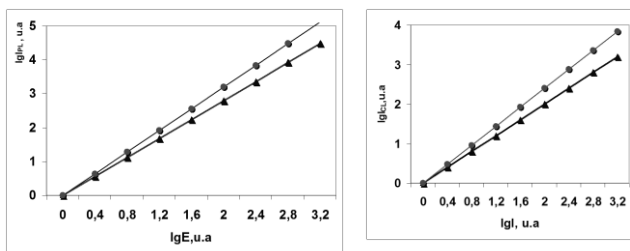


Fig. 1. Dependence of the integrated intensity of emission on the level of the excitation energy: 1 – the manganese content comprises  $6,2 \cdot 10^{19} \text{ cm}^{-3}$ ; 2 – the manganese content comprises  $1,9 \cdot 10^{20} \text{ cm}^{-3}$ .

1a – the photon excitation, 1b – the electronic excitation for  $\text{ZnIn}_2\text{S}_4:\text{Mn}$ ,  $T = 80\text{K}$ .

The analysis of the presented results made it possible to determine the function  $I_{ir} \approx E^\alpha$  in the explicit form, where in the case of the photon excitation  $\alpha = (1,3 \div 1,8)$  depending on the manganese concentration (the

higher manganese concentration in the compound the more value of  $\alpha$ ) for the electronic excitation  $\alpha = (0,96 \div 1,01)$  and  $\alpha$  also increases when manganese concentration increases. So, we determined experimentally that the form of the spectral region studied does not almost change. Without taking into account the other components of the spectrum, the data obtained experimentally were compared with the results obtained for the unalloyed material.

The radiation spectra composition of the doped samples showed the line with the maximum at  $1,91 \text{ eV}$ , which is absent in the spectrum of the unalloyed sample. In this work the modifications of this line under the effect of the temperature and manganese concentration are mainly analyzed. In Fig. 2 the emission spectrum region of  $\text{ZnIn}_2\text{S}_4(\text{III})$  polytype sample doped by manganese with the concentration of  $6,2 \cdot 10^{19} \text{ cm}^{-3}$  obtained at 300K is shown.

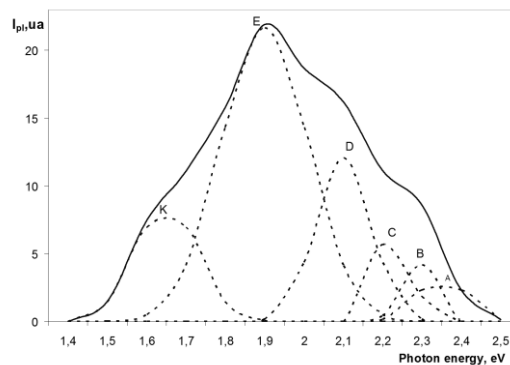


Fig. 2. The emission spectrum region of  $\text{ZnIn}_2\text{S}_4(\text{III})$  polytype sample doped by manganese with the concentration of  $6,2 \cdot 10^{19} \text{ cm}^{-3}$  at 300K. The full curve shows the experimental spectrum, broken curve - the special features of elementary spectra calculated according to the Alentsev – Foch method [7].

The following specific features were experimentally found for this emission band. The emission intensity of this band increases in proportion to the increase of ligand concentration; for example, the manganese concentration increased threefold; accordingly, the intensity of the recombination processes increases threefold, which can be attributed to the threefold increase in the concentration of recombination centers formed by manganese which are contained in the respective sample. The energy position of this band does not change when the Mn concentration in the crystal increases; however, the shape of the emission band significantly changes under the same conditions, and a considerable increase in the half-width of the band under study is simultaneously recorded.

The maximum of emission band, which, in our opinion, is caused by the presence of manganese in polytype being investigated, does not shift with a temperature change in the interval from 80 to 300K. The analogous situations, described above, are known from the literature for a number of other compounds [7]. The maxima of elementary spectral structures correspond to the special features registered experimentally on the curve of the outline inclination on the left and on the right of this section. The energy positions of these special features maxima are the following:  $A(E_{\text{max}} = (2,25 \pm 0,05) \text{ eV})$ ;

B( $E_{\max}=(2,17\pm 0,05)\text{eV}$ ); C( $E_{\max}=(2,14\pm 0,05)\text{eV}$ );  
 D( $E_{\max}=(2,02\pm 0,05)\text{eV}$ ); E( $E_{\max}=(1,91\pm 0,05)\text{eV}$ );  
 K( $E_{\max}=(1,61\pm 0,05)\text{eV}$ ).

In Fig. 3 the emission spectrum structure of the sample with the introduced admixture concentration of  $6,2 \cdot 10^{19} \text{ cm}^{-3}$ , registered at the temperature of 80K is shown.

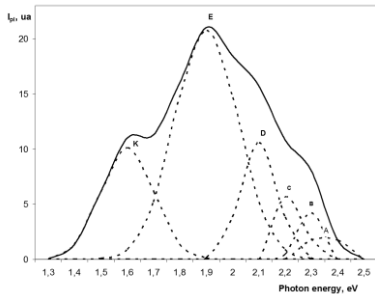


Fig. 3. Radiative spectrum of the  $\text{ZnIn}_2\text{S}_4$  polytype doped with manganese with the concentration of  $6,2 \cdot 10^{19} \text{ cm}^{-3}$ , at 80K.

It is evident from the experimental results that the energy positions of the above indicated lines maxima do not change. The temperature decrease up to 80K leads to an increase in the emission intensity of approximately 3 times with the simultaneous retention of the energy positions of all spectral special features obtained at 300K.

In Fig. 4 the emission spectrum region of the  $\text{ZnIn}_2\text{S}_4$  polytype doped with manganese with the concentration of  $1,9 \cdot 10^{20} \text{ cm}^{-3}$  at the temperature of 80K is shown.

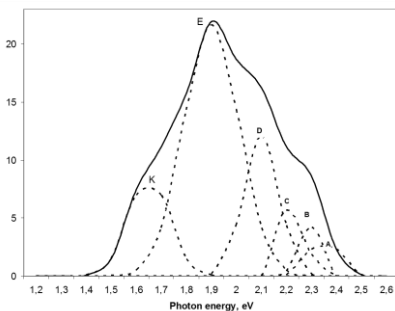


Fig. 4. Spectral region of emission of the  $\text{ZnIn}_2\text{S}_4$  polytype doped with Mn with a concentration of  $1,9 \cdot 10^{20} \text{ cm}^{-3}$  at the temperature of 80 K.

An increase in the concentration of the doping element (3.06 times) in this case also leads to an increase of three times in the emission intensity. This indicates a

significant change in the shape of the spectral region, maintaining the energy position of all specified spectral features for a manganese concentration of  $6,2 \cdot 10^{19} \text{ cm}^{-3}$ , as shown in Fig. 3.

## CONCLUSION

1. The basic special features of the radiative recombination spectra of the  $\text{ZnIn}_2\text{S}_4$  polytype doped with manganese are analyzed.
2. It is shown that manganese impurity in  $\text{ZnIn}_2\text{S}_4$  strengthens the emitting recombination processes.
3. A number of spectral lines with the energy peaks at 1,6; 1,91; 2,02; 2,14; 2,17 and 2,25 eV, which correspond, in our opinion, to the intra-center transitions are recorded experimentally.
4. The theoretical calculation of such optical transitions is a fairly complicated task which requires an additional study.

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