SPECIFIC FEATURES OF RADIATIVE RECOMBINATION SPECTRA OF $ZnIn_2S_4$ SINGLE CRYSTALS

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Abstract

Radiative recombination spectra of Mn-doped zinc tioindat 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 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 the Alentsev–Foch method.

1. 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. 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 worthily applied [6]**.** This situation takes

place because of a number of 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 effect of various ligands as well as control of the structure of intrinsic defects [7]. 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 [8, 9]. 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 effect of two different forms of excitation—electronic and photonic—were analyzed in this work. Radiation spectra were studied depending on temperature, manganese concentration, and excitation process.

2. Results and discussion

Radiative recombination spectra of $ZnIn_2S_4$:Mn single crystals with different manganese concentrations were obtained using a standard procedures at 80 and 300 K. The samples under study were grown in a closed volume from the vapor phase by the method of chemical transport reactions; elementary components were taken in a stoichiometric proportion. The growth technology is described in [3].

This method makes it possible to combine the synthesis and growth reactions with the simultaneous doping with manganese in a single technological cycle. The studied samples were perfect single crystals with a thickness of 250–300 μm and an area of up to 1 cm^2. The manganese concentration in the studied models was varied in a range of $5 \cdot 10^{18}$ to $2.5 \cdot 10^{20}$ cm^{-3}. The samples exhibited *n*-type conductivity, which was determined from the analysis of galvanomagnetic effects.

For the samples, the absorption spectra at temperatures of 80 and 300 K were preliminarily measured. The band gap was determined according to the form of the absorption spectra using a standard procedure. These experiments made it possible to obtain the following data for the band gap of the studied compounds:

$$E_g\,(300\ \text{K}) = 2.8 \pm 0.05\ \text{eV}$$
$$E_g\,(80\ \text{K}) = 2.95 \pm 0.05\ \text{eV}$$

The radiative recombination spectra of the doped compounds were measured from the plates with an area of 0.3 cm^2 and a thickness of 200–300 μm in two excitation modes: the one induced by an electron beam with an energy of up to 60 keV and a current density of up to 10^{-2} A cm^{-2} and photon excitation with an excitation quantum energy (laser) of 3.67 eV (λ = 337 nm).

The photoluminescence and cathodoluminescence spectra were recorded at two temperatures. To reveal the specific character of the electronic or photon process of excitation,

the experimental dependences of integrated intensity on the mode and level of excitation were studied.

Figures 1a and 1b show the integrated intensities for the different levels and modes of excitation: (a) photon excitation and (b) electron excitation. The integrated intensities depending on levels and modes of excitation were obtained at a temperature of 80 K for two samples with different manganese concentrations.

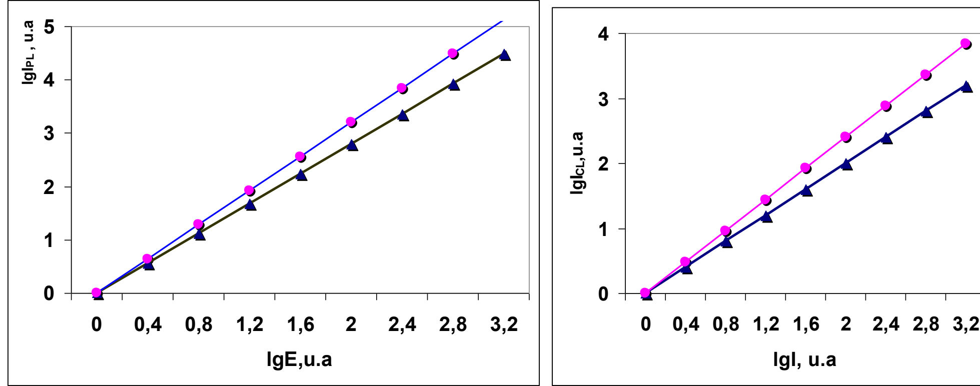

Fig. 1. Dependence of the integrated intensity of emission on the level of excitation energy: the manganese content is (*1*) $6.2 \cdot 10^{19}$ cm^{-3} and (*2*) $1.9 \cdot 10^{20}$ cm^{-3}; (a) photon excitation and (b) electron excitation for $ZnIn_2S_4$:Mn, $T = 80$ K.

The analysis of the results made it possible to determine the function $I_{ir} \approx E^{\alpha}$ in the explicit form, where, in the case of photon excitation, $\alpha = 1.3–1.8$ depending on the manganese concentration (the higher manganese concentration in the compound, the higher the value of α); for electron excitation, $\alpha = 0.96–1.01$ and α also increases with increasing manganese concentration. Thus, it was experimentally determined that the form of the studied spectral region hardly changes.

Neglecting other components of the spectrum, the experimental data were compared with the results for the undoped material. In the composition of the emission spectra of the doped sample, a spectral line peaking at 1.91 eV was observed; it was absent in the undoped sample. In this study, the modifications of this line under the effect of temperature and manganese concentration are mainly analyzed. Figure 2 shows the emission spectrum region of $ZnIn_2S_4$(III) polytype sample doped with manganese with a concentration of $6.2 \cdot 10^{19}$ cm^{-3}, which was recorded at 300 K.

The radiative recombination spectrum in the studied spectral range has a complex structure. This complex spectrum has the form of a band with an energy peak at 1.91 ± 0.003 eV, but it is absent in the spectrum of the undoped sample and exhibits unusual behavior; that is, it does not undergo a temperature shift in a temperature range of 80–300 K; its intensity increases with increasing manganese concentration. This spectral line is absent in the spectra of undoped material. In this study, in principle, these band modifications under the effect of temperature and manganese concentration variations are analyzed. It is evident from the results that this spectral region has a complex form and a fairly high half-width. It is shown that different optical transitions caused by manganese make the greatest contribution to this spectrum. Subsequently, the known method of dispersion of a complex spectrum onto simple spectral bands proposed by Alentsev and Fok [7] was used. The complex spectrum is decomposed into a number of specific

features represented in the figure by broken curves and designated by A, B, C, D, E, and K, respectively.

The following specific features were experimentally found for this emission band. The emission intensity of this band increases with increasing ligand concentration; for example, the manganese concentration increases 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 with increasing Mn concentration in the crystal; 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.

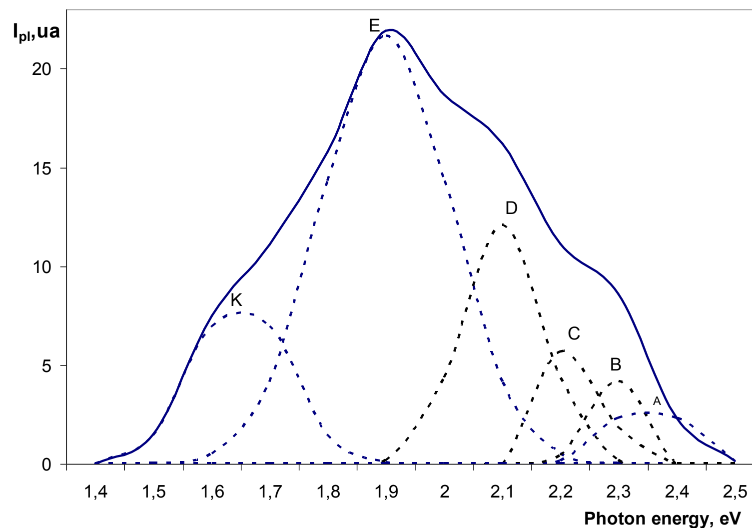

Fig. 2. Emission spectrum region of $ZnIn_2S_4$(III) polytype sample doped with manganese with a concentration of $6.2 \cdot 10^{19}$ cm^{-3} at 300 K.

The maximum of emission band, which, in our opinion, is caused by the presence of manganese in the studied polytype, is not shifted with changing temperature in a range of 80 to 300 K. Similar situations are known from the literature for a number of other compounds [6]. The maxima of elementary spectral structures correspond to the special features experimentally recorded in the curve along the contour of the slope to the left and to the right of this region. The energy positions of of the maxima of these features are as follows: A(E_{max} = 2.25 ± 0.05 eV); B(E_{max} = 2.17 ± 0.05 eV); C(E_{max} = 2.14 ± 0.05 eV); D(E_{max} = 2.02 ± 0.05 eV); E(E_{max} = 1.91 ± 0.05 eV); and K(E_{max} = 1.61 ± 0.05 eV).

Figure 3 shows the emission spectrum structure of the sample with the introduced admixture with a concentration of $6.2 \cdot 10^{19}$ cm^{-3} recorded at a temperature of 80 K.

It is evident from the experimental results that the energy positions of the above maxima do not change. A decrease in temperature to 80 K leads to approximately a threefold increase in the emission intensity, while maintaining the energy positions of all spectral features recorded at 300 K.

Figure 4 shows the emission spectrum region of the $ZnIn_2S_4$ polytype doped with manganese with a concentration of $1.9 \cdot 10^{20}$ cm^{-3} at a temperature of 80 K.

An increase in the concentration of the doping element (3.06 times) in this case leads to an

increase in the emission intensity also by a factor of 3. This indicates a significant change in the shape of the spectral region, while maintaining the energy position of all the specified spectral features for a manganese concentration of $6.2 \cdot 10^{19}$ cm^{-3}, as shown in Fig. 3.

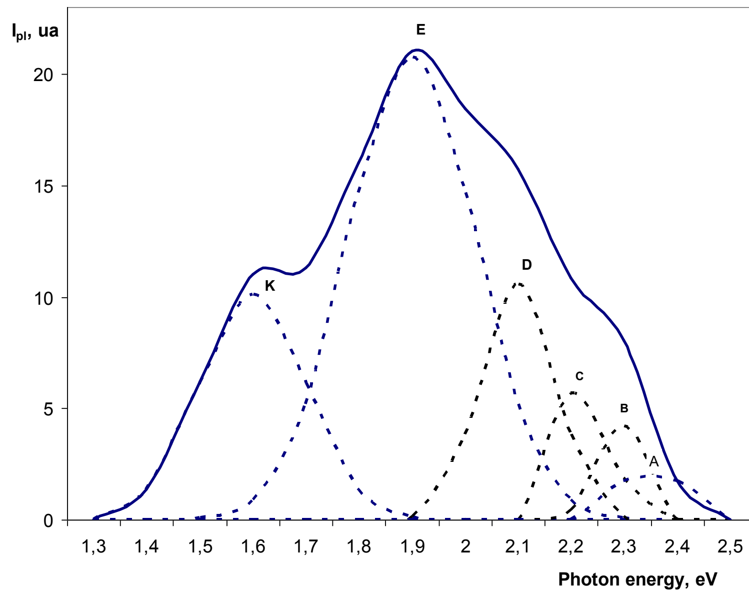

Fig. 3. Radiative spectrum of the $ZnIn_2S_4$ polytype doped with manganese with a concentration of $6.2 \cdot 10^{19}$ cm^{-3} at 80 K.

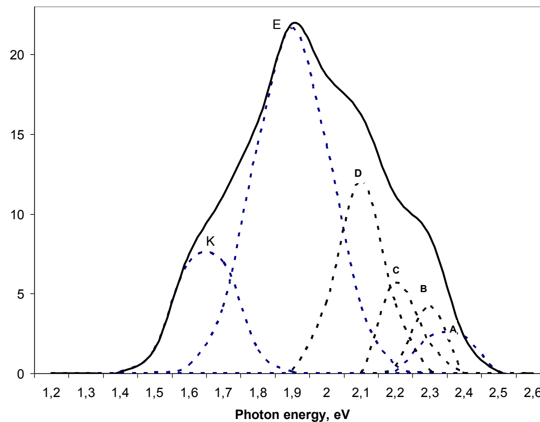

Fig. 4. Emission spectrum region of the $ZnIn_2S_4$ polytype doped with Mn with a concentration of $1.9 \cdot 10^{20}$ cm^{-3} at a temperature of 80 K.

3. Conclusions

(1) The basic special features of the radiative recombination spectra of the $ZnIn_2S_4$ polytype doped with manganese have been analyzed.
(2) It has been shown that a manganese impurity in $ZnIn_2S_4$ strengthens the emission recombination processes.
(3) A number of spectral lines with 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 have been experimentally

recorded.

(4) A theoretical calculation of these optical transitions is a fairly complicated problem which requires a further study.

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