

LUMINESCENT PROPERTIES OF Sb-DOPED ZnSe SINGLE CRYSTALS

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Abstract

Photoluminescence (PL) spectra of ZnSe:0.1at%Sb single crystals are studied between 90 and 300 K. The samples are grown by the chemical vapor transport (CVT) method with iodine as a transport agent and doped with Sb impurity during the growth. A yellow PL band with a maximum at 2.16 eV (575 nm) at room temperature is observed for the first time. A model of a $(\text{Sb}_{\text{Se}}\text{I}_{\text{Se}})$ acceptor center with the energy level located at 0.52 eV above the valence band edge is proposed, and the mechanism of the formation of this yellow PL band under direct and indirect excitation is discussed.

1. Introduction

Radiative properties of ZnSe:Sb samples are studied in a series of papers [1–4]. The conclusions made in the papers about the effect of Sb impurity on the sample properties essentially differ, probably, due to the fact that the studied samples were grown by different methods and measured in different spectral ranges at different temperatures. For example, the authors of [1] argue that annealing of ZnSe samples in an Sb melt does not lead to the formation of Sb-based luminescence centers responsible for edge luminescence; however, it contributes to the “purification” of the samples from background impurities. At the same time, according to [2, 3], Sb impurity is considered to be responsible for the edge photoluminescence (PL) bands localized at 444, 450.5, 456.7, 461, and 463 nm. The PL bands localized at longer wavelengths at 550, 640, 760, and 820 nm are attributed to Sb impurity in [4]. Since the as-grown undoped ZnSe samples contain uncontrollable donor impurities of Group III elements in the unbound state (D_{Zn}), the authors consider $(\text{A}_{\text{Se}}\text{D}_{\text{Zn}})^{-}$ associative defects with various distances between the components to be responsible for the PL bands observed for ZnSe:Sb samples. At the same time, there are no bands in the PL spectra that can be attributed to $(\text{A}_{\text{Se}}\text{D}_{\text{Se}})^{-}$ centers [4]. Thus, it may be of interest to introduce D_{Se} donors to form $(\text{A}_{\text{Se}}\text{D}_{\text{Se}})^{-}$ luminescence centers and study their effect on PL spectra of the ZnSe:Sb samples.

2. Experimental

ZnSe and ZnSe:Sb samples were grown by the chemical vapor transport (CVT) method with iodine as a transport agent. An Sb acceptor impurity (0.01 at %) and Zn and Se components were loaded into quartz tubes, which were placed in a furnace so that the nutrient zone

temperature was 1180–1190 K and the crystallization zone temperature was 1165–1175 K. The purity of the chemical substances was as follows: 99.999% for Zn, Se, and Sb and 99.99% for I.

PL spectra were measured at 300 and 90 K in the wavelength range between 400 and 800 nm under excitation with laser radiation of 337 and 473 nm. The spectra were registered using a standard synchronous detection system with an MDR-23 monochromator and a FEU-100 photomultiplier and corrected for the spectral sensitivity of the detection system.

3. Experimental Results and Discussion

Figure 1 shows room-temperature PL spectra of ZnSe and ZnSe:Sb crystals excited with ultraviolet laser radiation ($\lambda_{\text{exc}} = 337$ nm). The PL spectrum of the undoped sample consists of three bands: the edge band localized at 2.68 eV (462 nm) with a full width at half maximum (FWHM) of 98 meV and two long-wavelength bands with maxima at 2.06 eV (600 nm) and 1.94 eV (640 nm) (Fig. 1, curve 1). A wide FWHM for the edge PL band suggests that it has a complex structure. According to [5], free excitons, as well as free-bound transitions involving shallow donor and acceptor impurities, can be responsible for this PL band. The introduction of Sb impurity into the samples decreases the edge PL intensity (Fig. 1, curve 2), apparently owing to a redistribution of the recombination channels in the doped sample, and does not change the shape and position of the edge PL spectrum.

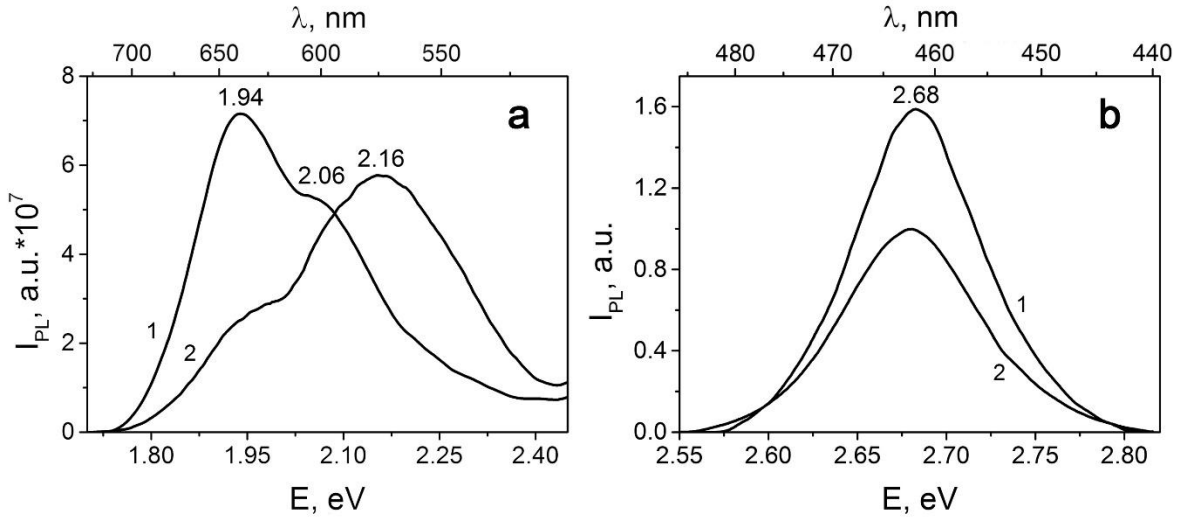


Fig. 1. (a) Long-wavelength and (b) edge PL spectra of (1) the undoped and (2) Sb-doped ZnSe samples. $\lambda_{\text{exc}} = 337$ nm ($h\nu_{\text{excit}} = 3.68$ eV). $T = 300$ K.

As temperature decreases to 90 K, the edge PL band is shifted towards high energies (2.77 eV, 447 nm) and narrows to 55 meV for both the undoped and Sb-doped samples (Fig. 2). According to [6], the ${}^4T_1-{}^6A_1$ and ${}^4T_2-{}^6A_1$ intracenter transitions within the Mn^{2+} ion are considered to be the main contribution to the formation of the long-wavelength PL band for the undoped sample at both 300 K (Fig. 1) and 90 K (Fig. 2). A short-wavelength wing of the band is probably caused by $[\text{I}_{\text{Se}}-(\text{V}_{\text{Zn}}\text{I}_{\text{Se}})]$ transitions or a Cu impurity [7].

The introduction of Sb impurity into the ZnSe samples changes the shape of the long-wavelength PL band, and the dominant maximum is now localized at 2.16 eV (575 nm) at 300 K (Fig. 1). Similarly to the undoped ZnSe sample, V_{Zn} and I_{Se} defects, as well as Cu and Mn ions, contribute to this PL band. However, the change in the shape of this PL band and the appearance of an additional maximum give reasons to suppose that a new recombination channel, “Sb-yellow radiation”, makes a major contribution to the band. It would appear reasonable that this radiation should be attributed to the Sb-based luminescence center in ZnSe. We suppose that the $(Sb_{Se}I_{Se})$ associative center, which forms the acceptor level located at ~ 0.52 eV above the valence band edge, can be this Sb-based luminescence center. The process of formation of this new PL band can be illustrated by two modes of excitation of the luminescence center: indirect (Fig. 3a) and direct excitation (Fig. 3b) depending on excitation energy.

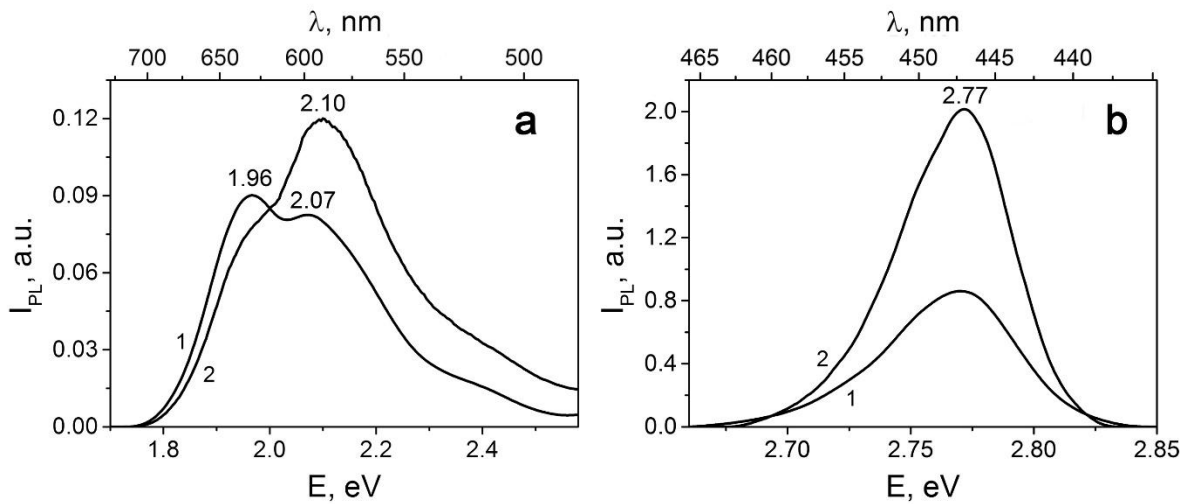


Fig. 2. (a) Long-wavelength and (b) edge PL spectra of (1) the undoped and (2) Sb-doped ZnSe samples. $\lambda_{exc} = 337$ nm ($h\nu_{excit} = 3.68$ eV). $T = 90$ K.

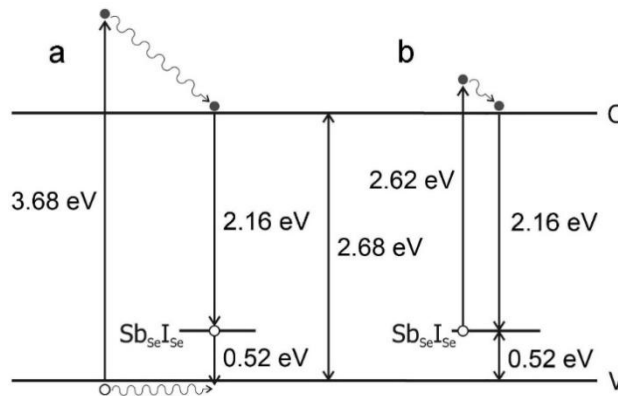


Fig. 3. Electron transitions under (a) indirect and (b) direct excitation of the $(Sb_{Se}I_{Se})$ luminescence center in the ZnSe:Sb single crystal.

λ_{exc} : (a) 337 nm ($h\nu_{excit} = 3.68$ eV) and (b) 473 nm ($h\nu_{excit} = 2.62$ eV). $E_g(300\text{ K}) = 2.68$ eV.

Under indirect excitation (Fig. 3a), after generation of nonequilibrium electron–hole pairs, the Sb-based acceptor center captures a valence hole. After that, a recombination of a nonequilibrium electron thermalized in the conduction band with this valence hole takes place. As a result, a respective photon is radiated. Under direct excitation of the luminescence center (Fig. 3b) with a photon energy below the band gap energy, a transition of the electron from the (Sb_{Se}I_{Se}) acceptor center deeply to the conduction band occurs. In this case, a recombination of the electron thermalized in the conduction band with a nonequilibrium hole localized at the (Sb_{Se}I_{Se}) associative center takes place. As a result, a respective photon is radiated.

For direct excitation of the (Sb_{Se}I_{Se}) luminescence center according to the scheme shown in Fig. 3b, the ZnSe:Sb samples were excited with laser radiation of 473 nm, which corresponded to an excitation energy of $h\nu_{\text{excit}} = 2.62$ eV, the value below the ZnSe band gap energy of 2.68 eV at room temperature. The PL spectra of the ZnSe and ZnSe:Sb samples at 300 and 90 K are shown in Fig. 4. It is evident that the yellow PL band is localized at the same wavelengths as those for indirect excitation of the luminescence center (Figs. 1, 2).

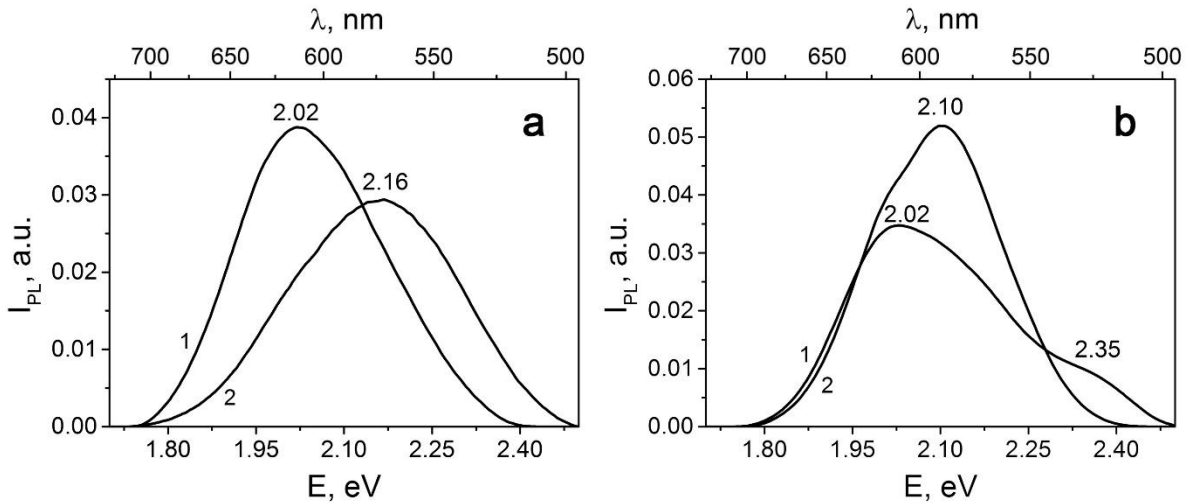


Fig. 4. Long-wavelength PL spectra of (1) the undoped and (2) Sb-doped ZnSe samples.

$\lambda_{\text{exc}} = 473$ nm ($h\nu_{\text{excit}} = 2.62$ eV). $T =$ (a) 300 and (b) 90 K.

The temperature evolution of the PL spectra of the ZnSe:Sb samples under indirect excitation is shown in Fig. 5. As the temperature decreases, the PL band increases in intensity and is shifted to 2.10 eV (590 nm). Since the band has a complex structure and consists of a series of elementary PL bands, this behavior can be attributed to the fact that, with decreasing temperature, the intensity of the long-wavelength components increases faster than that of the short-wavelengths components. As a result, the yellow PL band is shifted towards long wavelengths.

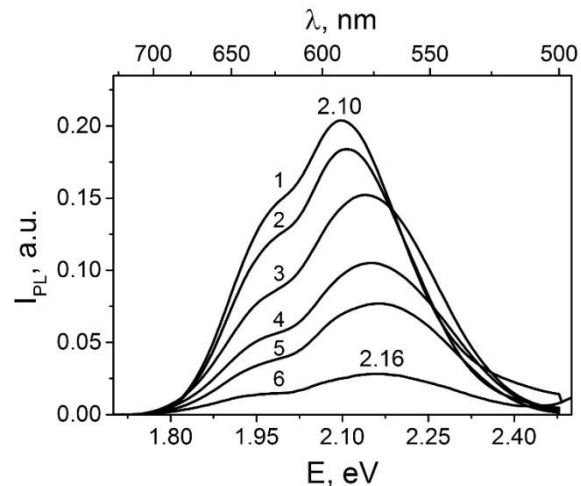


Fig. 5. Temperature evolution of the long-wavelength PL spectrum of the ZnSe:Sb sample. $T = (1) 90, (2) 130, (3) 180, (4) 220, (5) 250, \text{ and } (6) 300 \text{ K. } \lambda_{\text{exc}} = 337 \text{ nm (} h\nu_{\text{excit}} = 3.68 \text{ eV)}$.

4. Conclusions

A new PL band with a maximum localized at 2.16 eV (575 nm) at room temperature has been first found in the PL spectra of the ZnSe single crystals doped with Sb impurity during the growth by the CVT method with iodine as a transport agent. It has been assumed that this PL band is attributed to a $(\text{Sb}_{\text{Se}}\text{I}_{\text{Se}})$ associative center with the energy level located at $\sim 0.52 \text{ eV}$ above the valence band edge in the ZnSe:Sb samples. A mechanism of the formation of this PL band under direct and indirect excitation of the luminescence center has been proposed to interpret the band behavior with temperature variation.

Acknowledgments

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