INFRARED LUMINESCENCE OF GOLD-DOPED ZnSe CRYSTALS

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Long-wave photoluminescence (PL) spectra of n-ZnSe single crystals doped with Au in different concentrations are studied in the temperature range from 81 to 300 K. A narrow band of infrared (IR) radiation centred at 878 nm manifests itself in the low-temperature PL spectrum. The intensity of this band first increases and then decreases with increasing concentration of doping impurity. The nature of the luminescence centre, its structure and the mechanism of radiative recombination are discussed on the ground of complex investigation of luminescence properties of ZnSe:Zn:Au crystals. It is shown that the observed IR radiation is caused by recombination of free electrons with holes localised on associative acceptors, which contain native defects V_{Zn} and impurity defects Au_i. It is established that gold is a chemically amphoteric impurity in ZnSe crystals and forms both donor (Au_i) and acceptor (Au_{Zn}) centres.

1. Introduction

IR luminescence manifests itself in the PL spectra of zinc selenide single crystals doped with various acceptor impurities. For instance, the IR luminescence was observed for undoped ZnSe crystals (the PL bands at 1919 and 2138 nm) and the crystals doped with manganese (at 2667 and 3212 nm), nickel and phosphorus simultaneously (structural band at 2583 nm), and chromium (wide band at 2214 nm) [1]. Thin structure of the last band in the PL spectra of ZnSe:Cr crystals at 4.2 K was found by authors [2]; and the most intensive IR PL band was localised at 1000 nm. A set of phonon replicas at 1030, 1192, and 1327 nm were found on the low-energy fall of this band for the crystals with low doping level. The IR radiation in the region of 1000 nm was also observed for ZnSe crystals doped with transitive and alkaline metals such as Cu, Fe, and Li [2]. It was supposed that the nature of luminescent centre was the same irrespective of the doping impurity. The radiation band at 1078 nm was found in the low-temperature (34 K) IR PL spectra of ZnSe:P crystals [3]. As the sample temperature rose, the position of its maximum was unchanged and its intensity decreased under the exponential law with 40 meV activation energy of the PL intensity temperature quenching. The nature of the radiative centre and the mechanism of the IR radiation were not established.

Intensive radiation in the near IR PL spectrum (960÷980 nm) manifested itself for ZnSe crystals both undoped and doped with stibium, bismuth, and gold [4]. It was shown that the IR PL spectra for undoped crystals at 103 K consisted of three individual bands centred at 850, 920, and 980 nm, while the long-wave band with the maximum at 960 nm in the PL spectra for ZnSe:Au crystals consisted of the individual components centred at 870, 920, and 980 nm.

In that way, the analysis of literature data shows that the near IR PL spectra of both undoped ZnSe crystals and the crystals doped with various acceptor impurities consist of either narrow PL band at 1000 nm or wide complex PL band at (960÷980) nm.

Recently, [5] we have studied the electrical properties of ZnSe crystals doped with Au and other metals.

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In this paper are reported the photo-luminescence spectra of n-ZnSe single crystals doped with Au in different concetrations.

2. Experimental results and discussion

The PL spectra of ZnSe single crystals doped with gold during a long (100 h) high-temperature (950 °C) thermal treatment in Zn+Au melt were investigated in the temperature range from 82 to 300 K. The doping level was varied by changing of Au content in the melt from 0.01 to 10.0 at.%. Luminescence was excited either by radiation of nitrogen impulse laser ILGI-503 with 337 nm wavelength ($E_{excit} = 3.68$ eV) or by monochromatic light from a VSU-1 monochromator with a halogen lamp.

In the near IR region of the PL spectra of both undoped and Au-doped ZnSe crystals, a narrow band with a half-width of 25 meV manifests itself at 878 nm. The excitation was made with 440 nm wavelength light. This band in the PL spectra of both ZnSe and ZnSe:Zn crystals is dominant, while the intensity of wide bands in the visible long-wave region of the spectrum ((500÷700) nm) is weak (Fig. 1, curve 1). The doping of the crystals with gold leads to a redistribution between the intensities of the observed PL bands. The inset to Fig. 1 shows the IR PL band intensity (curve 5) and the ratio of the IR PL band intensity ($\lambda_{max} = 878$ nm) to the wide bands intensities ($\lambda_{max} = 594$ nm (curve 6) and $\lambda_{max} = 630$ nm (curve 7)) for the crystals with various dopant contents.

With increasing Au concentration, the intensity of the IR PL band first increases and then sharply decreases. The increase of the IR PL band intensity gives reasons to suppose that corresponding luminescent centre contains the Au-related impurity defect of donor type. We think, this defect is interstitial atom Au_i. Because of small ionic radius of Au atom ($R_i(Au)=1.37$ Å), gold impurity preferably forms Au_i defects at small Au concentrations and rapid cooling of the samples.

As Au concentration increases up to the higher values, Au atoms occupy mainly Zn vacancies and form Au_{Zn} acceptor defects. At the same time, the intensity of the IR PL band at 878 nm rapidly decreases (Fig. 1, inset, curve 5). This indicates the fact that Au_{Zn} defect is not a component of the luminescence centre. Intensities of the wide bands at 594 and 630 nm rapidly increase with increasing Au concentration in Zn+Au melt (Fig. 1, curves 2-4). Consequently, the ratio of the IR PL band intensity to the wide bands intensities decreases (Fig. 1, inset, curves 6, 7). It has been established that spectral position of the IR PL band is unchanged with increasing excitation radiation intensity. This fact gives reasons to attribute the observed IR luminescence to recombination of free electrons with holes localised on luminescent centres. If IR luminescence had been caused by recombination of donor-acceptor pairs, PL band would have shifted towards the short wavelengths with increasing excitation radiation intensity.
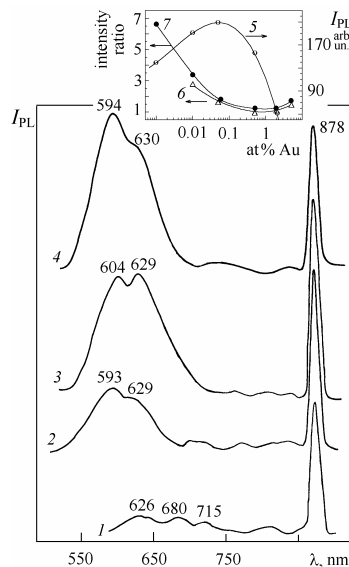

Fig. 1.   Long-wave PL spectra of ZnSe:Zn:Au crystals. $T = 84$ K. $\lambda_{excit} = 440$ nm. Au contents in Zn + Au melt, at%: 1–0, 2–0.01, 3–0.05, 4–0.5. (Inset): IR PL band intensity (5) and the ratios I_{878}/I_{594} (6) and I_{878}/I_{630} (7) versus Au content in Zn + Au melt.

With increasing excitation radiation wavelength, the IR PL band intensity increases, this band becomes narrower and shifts towards the long wavelengths (Fig. 2). Evidently, the IR luminescent centre is an associative centre. As the distance between the associate components decreases, the acceptor level approaches the valence band, because positive donor diminishes disturbing influence of negative acceptor on the lattice. The similar process takes place for the donor level.

We suggest that the near IR radiation of ZnSe:Zn:Au crystals is ascribed to the associative centre $(V_{Zn}^{--} Au_i^+)^-$. The donor component of this associative centre is ionised in the investigated temperature range. Hence, the associative defect can be regarded as a singly ionised acceptor. The associative centres $(V_{Zn}^{--} Au_i^+)^-$ with various distances between the associate components form a series of deep acceptor levels. Thus, the transitions of free nonequilibrium electrons to these acceptor levels take place.

According to the proposed model of the associative luminescent centre, increasing excitation radiation wavelength should result in consecutive excitation of the associative centres with increasing distances between their components. Consequently, the radiative transitions of free electrons to deeper acceptor levels of the associative centre take place with increasing excitation radiation wavelength, and the maximum of the IR PL band shifts towards the long wavelengths (Fig. 2, curve 1). As energy level of the luminescent centre moves away from the valence band absolute limit, the hole-binding energy increases, wave function becomes less fuzzy, and electron-capture cross-section decreases. As a result, the half-width of the IR PL band decreases.
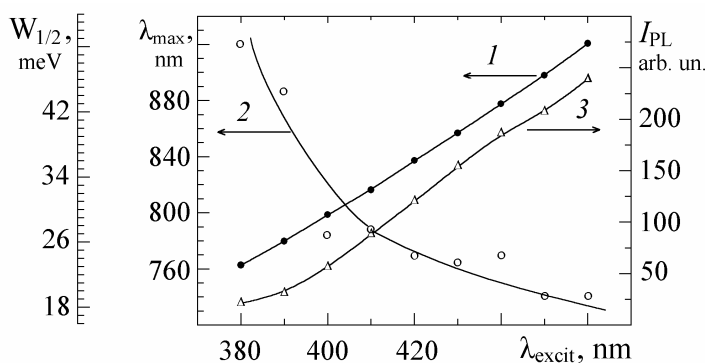

Fig. 2. IR PL band position (1), half-width (2), and intensity (3) versus excitation wavelength for the ZnSe:Zn:5 at% Au crystal. $T = 84$ K.
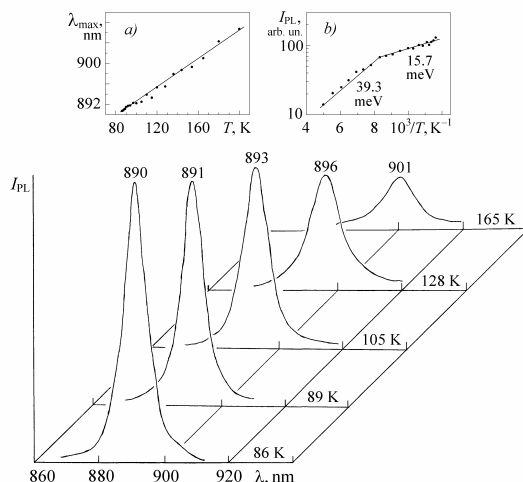

Fig. 3. IR PL spectra for as-grown ZnSe single crystal at different temperatures. (Inset a): IR PL band position versus temperature. (Inset b): IR PL band intensity versus temperature.

Thus, with increasing excitation radiation wavelength, the IR PL band both shifts towards long wavelengths and becomes narrower (Fig. 2, curves 1, 2). On the other hand, small electron-capture cross-section and large energy distance between the luminescent centre and the valence band absolute limit make difficulties for thermal capture of valence electron and reduce the probability of the PL band intensity temperature quenching. As a result, the IR PL band intensity should increase with increasing excitation radiation wavelength at fixed temperature (Fig. 2, curve 3).

The presence of the PL band with the maximum at 878 nm in the low-temperature (84 K) PL spectra of the as-grown undoped ZnSe single crystals confirms the validity of our assumption that native defect V_{Zn}^{--} is a part of the associative luminescent centre responsible for the IR luminescence. Fig. 3 shows the temperature influence on the IR PL spectra of the as-grown undoped ZnSe single crystal. As temperature increases, the maximum of the IR PL band shifts towards long wavelengths under the linear law in accordance with the temperature change of the ZnSe band gap (Fig. 3, inset a). The temperature quenching of this band intensity is characterised by two values of activation energy: the low-temperature value of 15.7 meV and the high-temperature value of 39.3 meV (Fig. 3, inset b). This fact may indicate the complex structure of the luminescent centre. We suppose that the near IR radiation of the as-grown ZnSe crystals is attributed to the associative centre $(V_{Zn}^{--} D^{+})^{-}$. Shallow non-controled substitution impurities Al_{Zn}, Ga_{Zn}, In_{Zn}, Cl_{Zn} or native defects V_{Se} can be the donors.

3. Conclusions

Finally, we think that the observed IR PL band in the luminescence spectra of Au-doped ZnSe crystals can be ascribed to radiative recombination of free electron with a hole localised on the associative acceptor. This associative acceptor contains the native acceptor defect V_{Zn}^{--} and the impurity donor defect Au_i^{+}. Gold is a chemically amphoteric impurity in ZnSe crystals and forms both donor (Au_i) and acceptor (Au_{Zn}) centres. However, Au_{Zn} substitution defect is not a component of the luminescent centre since the IR PL band intensity decreases with increasing Au concentration in Zn+Au melt, when the formation of Au_{Zn} defects is predominant.

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