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Emission characteristics of donor-acceptor pairs in ZnSe and CdS crystals

V.I.Oleshko, S.S.Vilchinskaya, V.M.Lisitsyn, V.I.Korepanov

National Research Tomsk Polytechnical University,
30 Lenina Ave., 634050 Tomsk, Russia

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The edge emission of undoped monocrystals of CdS and ZnSe was studied. It has been found that in pulse cathodoluminescence spectra of the crystals at 15 K consist of short-wave and long-wave series of edge emission bands with the equidistant structure. The temperature dependence of edge emission intensity in interval of 15–80 K and spectra of afterglow in interval 10^{-8} to 10^{-2} s were investigated.

Изучено краевое излучение нелегированных монокристаллов CdS и ZnSe. Установлено, что в спектрах импульсной катодолюминесценции кристаллов при температуре 15 К наблюдаются две серии полос краевого излучения с эквидистантной структурой — коротковолновая серия и длинноволновая. Исследована температурная зависимость краевого излучения в интервале 15–80 К и спектры послесвечения в диапазоне от 10^{-8} до 10^{-2} с.

I. Introduction

A_2B_6 compounds are promising materials in optoelectronics and infrared technologies. However, the data on luminescence centres in undoped CdS crystals have not been systematized, and are rather contradictory. In particular, one of the most challenging tasks is the determination of microscopic nature of the defects causing the edge emission in A_2B_6 semiconductors [1–6]. The recent studies of the edge emission have been mainly focused on spectral response characteristics, which is insufficient for the identification of its nature. This work summarizes the results of the study of the edge emission spectral-kinetic characteristics of undoped cadmium sulphide and zinc selenide with different history.

2. Material and methods

The hexagonal cadmium sulphide and cubic zinc selenide monocrystals were chosen for the investigation. The bulk crystals were obtained by Davydov-Markov method [7]. The CdS samples were in the form of a 2 mm thick plate, and they were cut from a block perpendicular to *C* optical axis. The cut surfaces were polished by mechanical means. The luminescence was excited by a heavy-current electron beam with the following parameters: the electrons average energy was ~0.3 MeV; half-amplitude duration ~10 ns. The electron beam energy density was regulated within 10^{-3}–10^{-2} J/cm^2. Residual gas pressure in the experimental chamber was ~10^{-4} Pa; temperature ~15 K. The sample was set at an angle 45° towards the electron stream propagation. Luminescence spectra were measured by means of the pulsing spectrometer in a spectral range of 450–850 nm. The glow of the sample was projected to the entrance slit of MDR-204 monochromator by means of a lens, and was registered by FEU-84 photoelectric multiplier and Tektronix TDS 2022 memory oscilloscope. Time resolution of the recording channel was ~ 10 ns, the spectral resolution was ~ 0.0015 eV.

3. Results

The study of the large group of undoped CdS and ZnSe crystals grown from vapour phase by the sublimation method showed that the edge emission was observed in majority of such crystals. The number of series and the band intensity depended on the history of crystals. Fig. 1 and 2 show the edge emission spectra of CdS No.1, measured at different times after the excitation pulse. As can be seen on the Figure, the distinct short wave series is observed within the range from 50 to 300 ns in the luminescence spectrum of the sample. The series has the maximum principal zero phonon line at $\lambda = 517$ nm, with its 1- or 2-LO phonon repetitions at 525 and 534 nm (Fig. 1). Energy spacing between separate peaks of the fine structure of the short wave series is equal to the LO-phonon energy of the CdS lattice (0.038 eV). Due to the quick attenuation of the short wave series in the edge emission spectrum of CdS No.1 crystal, the long wave series of equidistant emission lines is dominating after 1 μs, with the maximum principal line at $\lambda = 519$ nm and its 1-, 2-, 3-LO phonon repetitions at 527.5, 536 and 544 nm (Fig. 2). It was discovered, that the long-wave series in this sample is characterized by a prolonged afterglow ~ 10 s.

As is seen on Fig. 1 and 2, the edge emission lines eventually shift towards lower energies.

Fig. 3 shows time resolved edge emission spectra of two zinc selenide crystals of different history: ZnSe No.1 and ZnSe No.2. As is seen on Fig. 3, ZnSe No.1 sample provides one short-wave series of the edge emission with the maximum zero phonon line at $\lambda = 461.5$ nm, while ZnSe No.2 crystal provides two series of the edge emission: a long wave series and a short wave series, with maximum primary lines at $\lambda_1 = 462$ nm and $\lambda = 465$ nm, accordingly. Energy spacing between separate peaks of the fine structure of the short wave and the long wave series is equal to the LO-phonon energy of the ZnSe lattice (0.031 eV). With the increase in time, maxima of the long wave and the short wave series shift towards the long wave region.

The change of the edge emission spectrum of ZnSe No.2 indicates that short wave glow intensity is generally higher, while the attenuation time is shorter in comparison with the long wave series. The logarithmic representation of edge emission

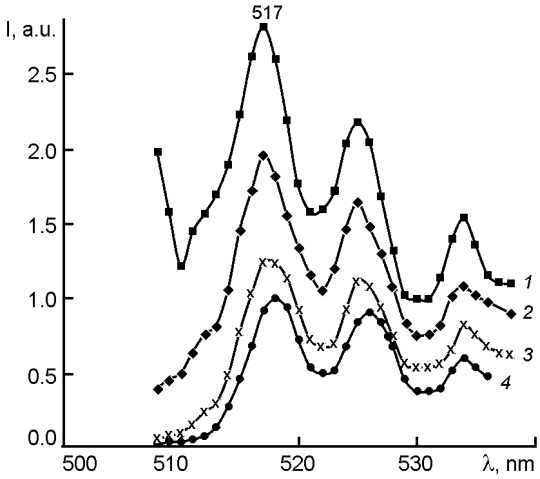

Fig. 1. Spectra of the short wave series of CdS No.1 edge emission; *1* — 50 ns, *2* — 100 ns, *3* — 200 ns, *4* — 300 ns.

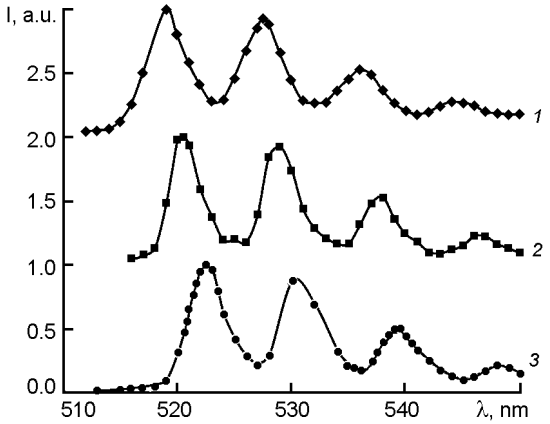

Fig. 2. Spectra of the long wave series of CdS No.1 edge emission; *1* — 1 μs, *2* — 20 μs, 3 — 50 μs.

attenuation curves demonstrated that attenuation kinetics were not exponential, and can hardly be approximated with exponential segments. It was only possible to conventionally define the quick primary segment and the slow subsequent segment. ZnSe No.2 sample demonstrated the decrease in the half width of separate lines of the edge emission equidistant structure with time.

We studied the dependence of the edge emission intensity on temperature. We found that as the temperature increased, the edge emission was subject to the strong thermal quenching (Fig. 4, 5). The quenching activation energy (λ_{max} ~ 519 nm, CdS No.1), calculated on the basis of the temperature dependence $\ln 1/\tau = f(1/T)$, equals to 0.03 eV, which corresponds to the donor level in cadmium sulphide.

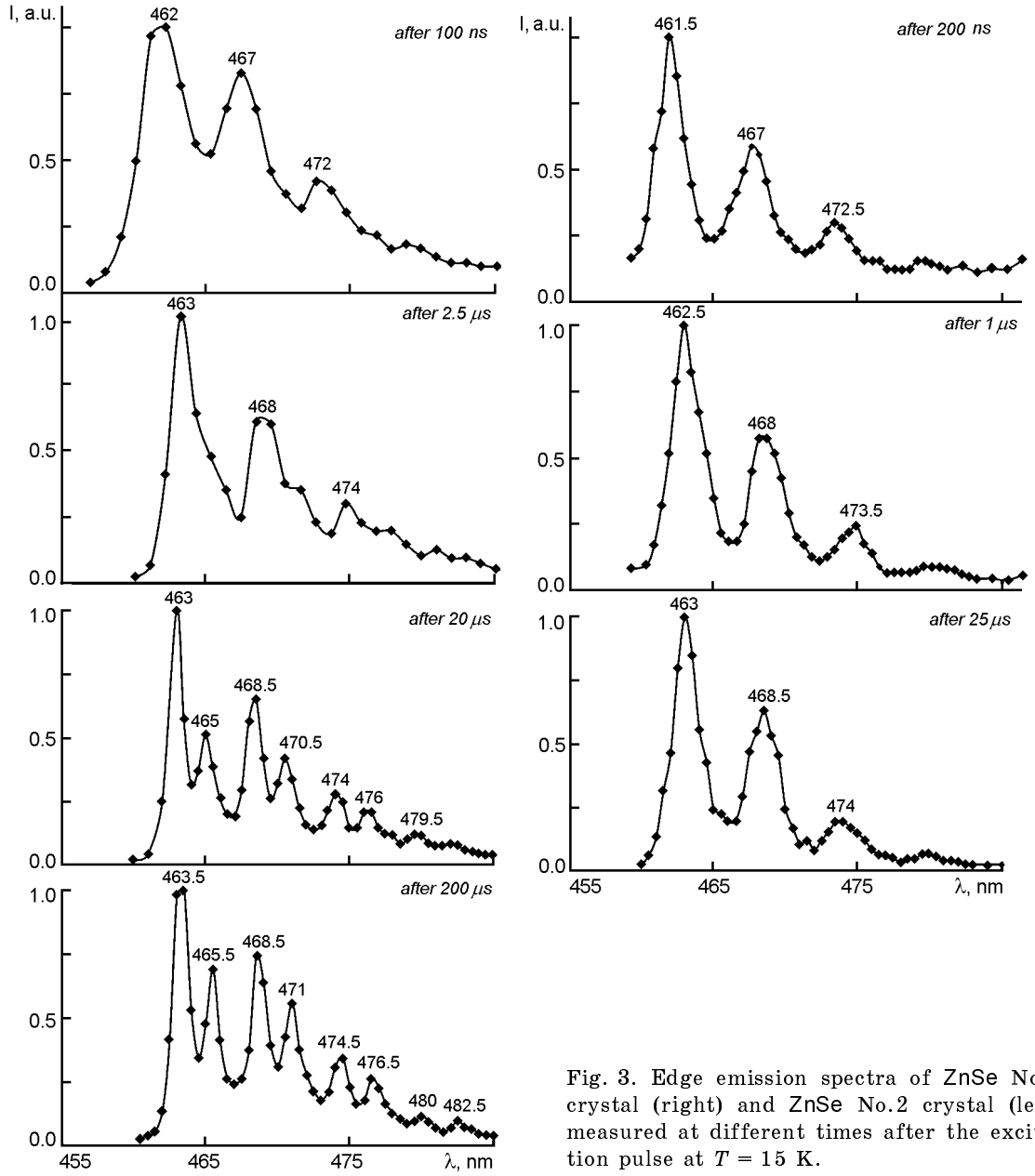

Fig. 3. Edge emission spectra of ZnSe No.1 crystal (right) and ZnSe No.2 crystal (left) measured at different times after the excitation pulse at $T = 15$ K.

4. Results discussion

All the observed patterns characterizing the CdS and ZnSe emission bands located near the edge of fundamental absorption are typical for the luminescence of donor-acceptor pairs [4–9], in particular, the presence of the equidistant structure in the emission spectrum characterizing the interaction with phonons of this lattice; the kinetics of donor-acceptor luminescence is not exponential; the difference of luminescence spectra measured at different times after excitation pulse. At starting moments after the excitation, recombination usually involves short-range pairs. Because of the low possibility of interimpurity transitions, long-range pairs illuminate later. As a result, with the time running after the excitation pulse, the short wave series and the long wave series bands of CdS No.1 shift towards the long wave (low energy) spectrum region for 0.005 and 0.014 eV accordingly, while the short wave series and the long wave series bands of of ZnSe No.1 and ZnSe No.2 shift for 0.01 eV. As the temperature grows in the range from 15 to 80 K, the edge emission intensity dramatically decreases (see Fig. 4, 5).

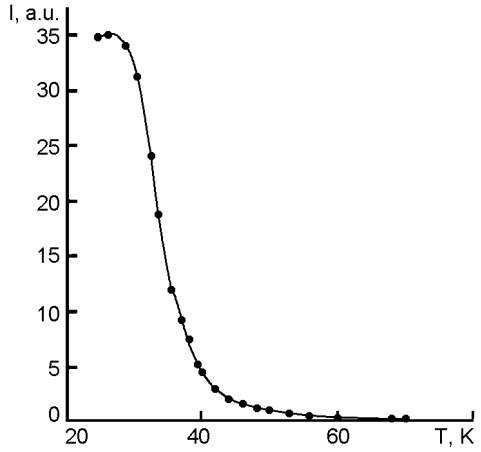

Fig. 4. Temperature dependence of CdS No.1 edge emission intensity (λ_{max} ~ 519 nm).

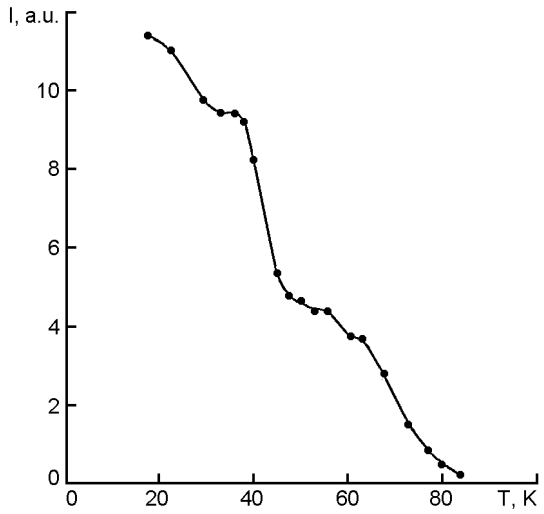

Fig. 5. Temperature dependence of ZnSe No.2 edge emission intensity (λ_{max} ~ 462 nm).

The issues of electronic transition mechanisms and the nature of defects responsible for various series of edge emission in A_2B_6 crystals are still a subject of many discussions [3–9]. It is believed that donors are shallow (for CdS, E_D = 0.024–0.032 eV, for ZnSe, E_D = 0.021–0.023 eV), while acceptors corresponding to both series are deep (for CdS, E_A = 0.14–0.15 eV), and having the common nature. The donor-acceptor pair emission occurs in the following manner. The nonequilibrium electron is captured by the ionized positively charged donor without emission, the electron hole is captured by the ionized acceptor, and then the emitting transition of the electron occurs from the donor to the acceptor.

The energy of the emitted photon is described with the following formula:

$$h\nu = E_g - (E_D + E_A) + e^2/4\varepsilon\varepsilon_0 R, \qquad (1)$$

where E_D and E_A are energy level positions of donor and acceptor levels relatively to the edges of nearest areas; R is the interimpurity distance; ε is the dielectric capacitance.

Formula (1) is presented with no account taken of the infinitesimal summand characterizing the difference between the interimpurity interaction and the Coulomb interaction for the closest pairs.

No investigations have been carried so far which would unambiguously describe the physical and chemical nature of the defects responsible for the various series of edge emission in undoped A_2B_6 crystals. It is supposed that both own defects and dopant atoms can act as donors and acceptors. A separate investigation of the nature of centres responsible for the edge emission of the crystals is required, which would surpass the scope of this work.

5. Conclusions

Using the pulse spectrometry method, we measured the spectral and kinetic parameters of the edge emission in undoped cadmium sulphide and zinc selenide crystals of different prehistory within the range from 10^{-8} to 10^{-2} s and a temperature of 15 K. It was found out that the number of edge emission series, their intensity correlation and spectral position are determined by the crystals prehistory. We measured the time shift of short wave and long wave series of the edge emission of actual CdS and ZnSe crystals after the excitation pulse. It was demonstrated that, depending on the crystal type, the maxima of edge emission lines shift to the long wave spectrum regions for 0.005–0.014 eV. The temperature dependence of the edge emission was investigated. It was revealed that when the temperature increases within a range of 15–80 K, the total intensity of the edge emission reduces more than by an order of magnitude. The results of the investigations support the donor and acceptor model of the centres responsible for the edge emission of undoped CdS and ZnSe crystals grown from the vapour phase by the sublimation method.

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Випромінювальні характеристики донорно-акцепторних пар у кристалах ZnSe і CdS

В.І. Олешко, С.С.Вільчинська, В.М.Лисицин, В.И.Корепанов,

Вивчено краєве випромінювання нелегованих монокристалів CdS і ZnSe. Встановлено, що у спектрах імпульсної катодолюмінесценції кристалів при температурі 15 К спостерігаються дві серії смуг краєвого випромінювання з еквідистантною структурою – короткохвильова серія і довгохвильова. Досліджено температурну залежність краєвого випромінювання в інтервалі 15-80 К і спектри післясвічення у діапазоні від 10^{-8} до 10^{-2} с.