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ANOMALOUS SERIES OF BANDS IN THE EDGE EMISSION SPECTRA OF CdS(O)

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The region of the edge emission spectrum of CdS(O) *single crystals with cadmium excess is examined. An anomalous series of equidistant bands with leading line at 514 nm and phonon replicas has been revealed. These bands grow in intensity with increase of the excitation density up to 10^{26}–10^{27} $cm^{-3}\cdot s^{-1}$ at 80 K, and the leading line of the series is observed even at 300 K. It is shown that luminescence is conditioned by the exciton spectrum in perfect bulk single-crystals of* CdO. *Some characteristics of this spectrum are presented, in particular, the dependence on temperature, excitation intensity, composition and size of the crystals, and the LO interaction. The results experimentally confirm the theoretically calculated magnitude of the direct band gap of* CdO.

Keywords: photoluminescence, edge emission, leading line, stoichiometry, excitation intensity, cadmium oxide, exciton.

INTRODUCTION

The close connection of edge emission (EE) with intrinsic point defects of gas-phase crystals of CdS(O) was discussed in [1–3]. The most intense EE was observed for stoichiometric samples. It shows up as a series of equidistant bands with leading line at 514–516 nm at 80 K and LO replicas. For crystals with maximum sulfur excess, EE is completely suppressed. With increase of the cadmium excess the bands of the series broaden, decrease in intensity, and the zero-phonon leading line is shifted to 516–525 nm. The observed shift is in agreement with the concentration of the oxygen background impurity in the crystals, well known from the analytical data.[1] These results were obtained from the cathodoluminescence spectra by using the technique described in [3] for an excitation intensity of 10^{22} $cm^{-3}\cdot s^{-1}$.

As was shown in [2–4], for stoichiometric crystals of CdS, at high excitation intensities EE is quenched. It is suppressed already for $G \geq 10^{23}$ $cm^{-3}\cdot s^{-1}$. The reason for this is saturation of luminescence centers since their density is around 10^{16} cm^{-3} [4].

As a counterweight to these data, in [5, 6] luminescence in the edge region of the spectrum was also observed at a high excitation density for CdS crystals with cadmium excess. The singular nature of this fact lies in the fact that the radiation was observed even at room temperature although usually EE in CdS is quenched already at 150–200 K [7, 8].

To clarify this question, we present here, as a follow-up to [2, 3, 9], results of a study on the nature of the series of equidistant bands in the *edge* region of the spectrum of gas-phase CdS(O) for high excitation intensity at different temperatures and compositions.

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[1] In this work we use the value for the A-exciton shift equal to 90 meV/mole% [O_S] from the data in [10] in accordance with band anticrossing theory.

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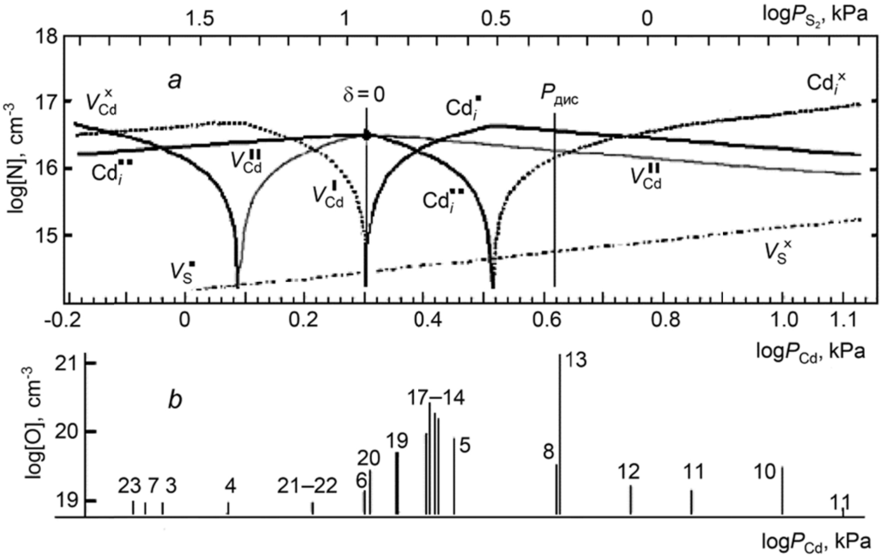

Fig. 1. Composition of the investigated single crystals of CdS as a function of growth conditions. Charge states of defects (–, – –, 0, + , ++) are denoted as (ǀ, ǀǀ, ×, ▪, ▪▪) respectively [7].

1. EXPERIMENT

Peculiarities of the crystal structure of samples with deviations from stoichiometry were examined. The crystal structure of the samples was investigated using a scanning electron microscope (SEM) [3]. All of the single crystals have block structure. Hexagonally oriented prisms – blocks – were prolate in the direction of the [0001] growth axis. We conditionally divide all of the crystals into three groups: samples with sulfur excess CdS·S, samples with cadmium excess CdS·Cd, and samples in the *stoichiometry region* – CdS.

A characteristic plot of the investigated crystals is given in Fig. 1. The type and concentration N of the intrinsic point defects versus the composition of the samples are shown in Fig. 1*a*; a line diagram of the powder pattern with numbers of the samples and oxygen concentration as a function of growth conditions of the crystals at 1100°C [3] is presented in Fig. 1*b*.

Under conditions of maximum sulfur excess CdS·S the crystals grow with a high concentration of cadmium vacancies (Fig. 1*a*), which easily coagulate and give rise to numerous pores. The ratio of enthalpies of formation of SO_2, CdO, and CdS (–71, –60.9, and –34.5 kcal/mole) underlies the preferred formation of SO_2 as the strongest compound. Gaseous sulfur oxide removes oxygen from the crystal, which also promotes the formation of pores.

The stoichiometry region corresponds to crystal growth under minimal sulfur vapor pressure. This is the region between the points: with stoichiometry δ = 0 and dissociation pressure CdS P_{dis} (Fig. 1*b*, No. 19–No. 5). Such crystals already contain a cadmium excess. SEM studies of the microstructure and microcomposition showed that the crystals of this group are very homogenous. The predominant point defects $Cd_i^{\bullet}$ were stabilized by dissolved oxygen O_S, which enters into the sulfur lattice sites during growth.

Crystals with a large Cd excess display *a layered inhomogeneity* of their volume in the SEM images. Precipitation of nanoparticles in the (0001) planes is a result of decay of the CdS(O)·Cd solid solution upon cooling from the growth temperature. The structure can become unstable upon aging, annealing, or radiative action, which leads to precipitation on the surface of pure cadmium.

Photoluminescence with shallow depth of the information layer is a promising method for examining the defect formations on the surface. Photoluminescence spectra were recorded at temperatures of 80 and 300 K and excitation by

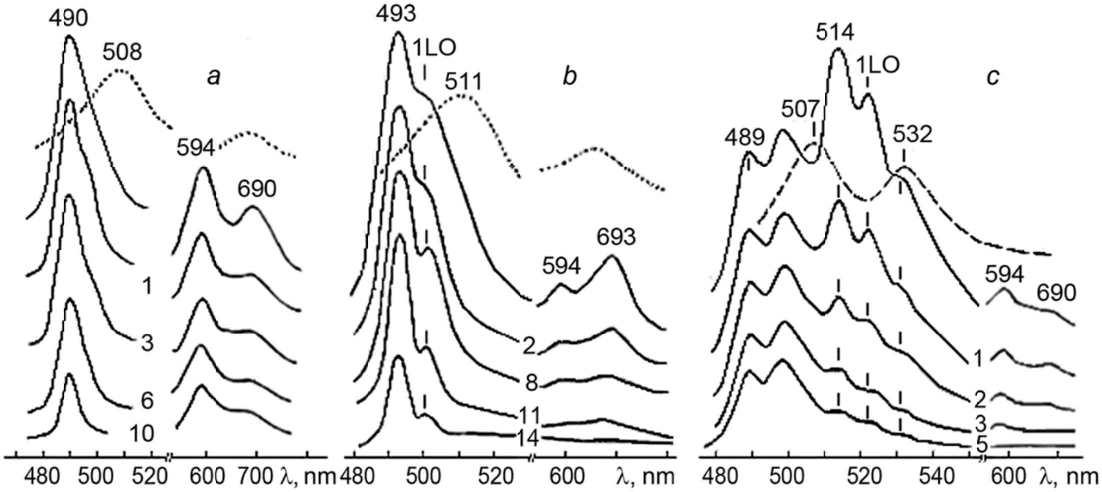

Fig. 2. Photoluminescence spectra at 80 K (solid curves) and 300 K (dotted curves) of single crystals with sulfur excess CdS·S (*a*, No. 23), cadmium excess CdS·Cd (*c*, No. 13), and in the stoichiometry region (*b,* No. 17). The maxima of the curves are indicated in nanometers. The numbers alongside the curves indicate the number of filters used to record the spectrum.

a 337.1-nanometer nitrogen laser with a pulse power of 4 kW, pulse duration of 10^{-8} s, and pulse repetition rate of 100 Hz. A set of filters was used, ensuring beam attenuation by a factor of 0.7 per filter. This technique allowed us to regulate the excitation density in the interval $G = (1\cdot10^{25}–7\cdot10^{27})$ $\text{cm}^{-3}\cdot\text{s}^{-1}$ [11].

2. RESULTS AND DISCUSSION

Photoluminescence spectra for the three basic groups of CdS(O) crystals are shown in Fig. 2. The spectra were measured from the blue exciton band up to the red band of the self-activated (SA) luminescence 600–700 nm, i.e., they include the green region which is characteristic for the EE of CdS. As it turned out, the general features of all the spectra are: 1) the absence of a spectral shift of all the bands with increase of the excitation density; 2) a shift of the A-exciton at 489–493 nm with the oxygen concentration in agreement with analysis and also with variation of the width of the band gap 90 meV/mole % [O_S] in agreement with [10]; 3) the width of the exciton bands of CdS(O) increases by a factor of 1.5–1.7 with increase of the excitation intensity, but their intensity increases within the limits of an order of magnitude; 4) the shift with temperature of the A-exciton of CdS(O) 489–493 nm is equal to $(4–5)\cdot10^{-4}$ eV/deg [1–3].

As can be seen from Fig. 2*a*, luminescence in the EE region at 80 K is absent for the CdS·S crystals. This luminescence is also not obvious for the samples in *the stoichiometry region* against the background of the CdS(O) exciton bands (Fig. 2*b*).

For the CdS·Cd crystals (Fig. 2*c*) in the edge region there arises a series of equidistant bands with leading line at 514 nm and LO phonon replicas at 522 and 531 nm (80 K), which increases abruptly with increase of the excitation density. At room temperature the leading line shifts to 532 nm. With increase of the excitation density the bands are narrowed, but their intensity grows more rapidly than that of the exciton bands of CdS(O). The spectral position of the bands of the series does not vary with excitation density and does not depend on the dissolved oxygen concentration, which does affect the exciton spectrum of CdS(O). It is specifically this group of bands that were considered in previous works to be the main EE series of CdS due to complexes of intrinsic defects [5, 6].

As the only one, the green band at 525–530 nm at 300 K was also observed in cathodoluminescence spectra of CdS(O) under high excitation intensity. The measured characteristic decay time of the 530-nm band is less than 20 ns [2, 3, 12], which is typical for exciton luminescence. These data were obtained, in particular, during measurent of pulsed cathodoluminescence at an excitation rate of ~10^{26} $\text{cm}^{-3}\cdot\text{s}^{-1}$ for a beam energy of 0.2 J/cm^2, when the beam

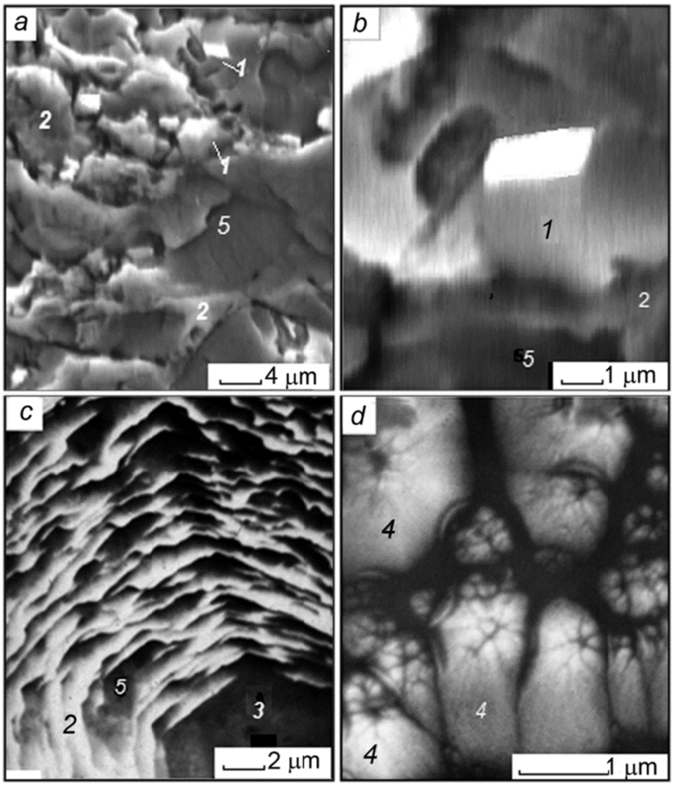

Fig. 3. Photomicrographs of crystals after etching, taken in the secondary emission mode of the SEM at 20 kV.

grazed the surface of the crystal. After exposure to radiation, precipitation of Cd on the surface and its oxidation to CdO were detected by SEM.

The possibility of forming CdO on the surface of unirradiated crystals is unclear. Additional information was provided by visual observation of the crystal surface at the time the electron beam was acting on it during SEM. Hexagonal-block single crystals under the action of the SEM beam glow with red light while individual point regions radiate bright green light. Blue exciton luminescence of CdS(O) as the basic emission of the investigated sample also could contribute to the luminescence of the entire surface, but not of the point sources of green emission. In the photoluminescence spectra these point regions of luminescence could be compared only to the 530-nm green band at 300 K or the corresponding series with leading line at 514 nm at 80 K.

An additional SEM study of peculiarities of the structure of crystals with Cd excess was performed. Some of the results are presented in Fig. 3.

As we have already mentioned, in the SEM observations of the interior of the CdS·Cd crystals, a layered contrast is observed in planes perpendicular to the growth axis. The layered inhomogeneity of CdS·Cd is associated with a non-uniform distribution of oxygen and cadmium in such crystals (*2*). Figure 3*c* shows an etch pit with a flat bottom (*3*).[2] Such pits are formed only on the cadmium-surface side and graphically illustrate the layered inhomogeneity of the composition of the crystal. Etching preferentially dissolves defect layers (*5*), while leaving intact the more pure and structurally perfect layers (*2*).

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[2] Details of the structure are revealed by etching slices of single crystals grown on the crystal seed by the Markov–Davydov vapor-growth technique. For CdS, solvents were used based on HCl 50% with polishing additives (e.g., Cr_2O_3). Etching was done at 300 K for 12 min.

Figure 3*a* shows the etched surface of single crystal No. 13 (see Fig. 1) from the cadmium side without an etch pit – 0001 layers (*2*). A detailed consideration of this image reveals a number of nascent little cubes (*1*). CdO crystals have a cubic shape in distinction to the hexagonal structures of Cd and its sulfide. In the pile-ups identification of the oxide is sometimes possible (using SEM and methods of light transmission microscopy)).[3]

Etching of CdS·Cd from the sulfur side $000\overline{1}$ (Fig. 3*d*, crystal No. 10) proceeds more slowly, separating out the tops of the hexagonal segmented blocks (*4*). The columnar growth of the blocks presupposes the passage of screw dislocations along the block axis with segregation on them of cadmium. At those places where the dislocations make their way to the surface, an ejection of finely dispersed Cd was observed in a state of progressive oxidation on the surface. The average atomic numbers of CdO (28) and CdS (32) differ noticeably, which enables contrast to be observed in the SEM images although the small size of the oxide formations hinders a determination of their composition.

Note that for the crystals with a cadmium excess that we investigated, the spectral position of the photoluminescence bands of the series with leading line at 514 nm (80 K) is quite stable. Obviously, unstrained perfect sulfur-free crystallites of CdO are formed during growth on the surface. The magnified image in Fig. 3*b* shows a CdO cube (*1*) that has grown on the surface of a purer 0001 layer. The underlying layers (*5*), enriched with oxygen and cadmium, are the source of the growth of such crystals. Formation of CdO microcrystals takes place, apparently, during cooling from the growth temperature of 1100°C and subsequent aging.

If the oxide segregates on the dislocations, then it is possible to include a small amount of sulfur and detect the exciton band of CdO(S), shifted in agreement with band anticrossing theory toward longer wavelengths, specifically to 535–537 nm (300 K). For nanocrystallites of CdO, in agreement with [2, 3], the position of the exciton band was shifted to 525 nm (300 K) as a consequence of quantum size effects. The absence of these bands in the spectra of the investigated CdS·S crystals with sulfur excess confirms their nature.

CONCLUSIONS

The photoluminescence band observed in CdS·Cd crystals at ~530 nm (300 K) correlates with the width of the direct band gap of CdO [11, 14, 15]. The series of equidistant photoluminescence bands with leading line at 514 nm (80 K) and LO replicas, described here for the first time, corresponds to the allowed exciton spectrum of sufficiently perfect crystals of CdO. The results obtained here allow us to define the variation of the width of the CdO band gap with temperature ($3.7\cdot10^{-4}$ eV/deg), the energy of the LO phonons (~35 meV), and the spectral position of the exciton bands for unstrained bulk crystals. Identification of this series provides experimental confirmation of the theoretically calculated value of the direct band gap of CdO.

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[3] Note that the above-considered crystal No. 13 does not belong to the stoichiometry region. It was grown not under minimal sulfur pressure, but under minimal cadmium pressure, at the CdS/CdO phase equilibrium boundary. Its oxygen content was on the order of 10^{21} cm^{-3} due to the presence of CdO.

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