

## ORANGE LUMINESCENCE OF DONOR–ACCEPTOR PAIRS IN CdS:Ag:Cl

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**Abstract**—The effect of preparation conditions (impurity concentration, partial vapour pressure of components, firing temperature) on the shape of the orange photoluminescence band in CdS:Ag:Cl is investigated. It is shown that the shape of the O-band may be treated as a superposition of two different bands for pure associated and distant DA pairs with peak positions 2.08 eV and 1.94 eV, respectively. Possible role of various preparation conditions on the distribution of DA pairs is discussed.

**Keywords:** Photoluminescence, donor–acceptor pairs, deep levels, PL band shape, preparation conditions, CdS.

### 1. INTRODUCTION

The deep radiative recombination centres in II–VI compounds are often connected with donor–acceptor (DA) complexes [1–9]. But there are still several problems concerning mainly the recombination mechanism in these centres. First of all, because of the deep levels the recombination probabilities for distant pairs must be quite small. At the same time many observable effects of distant DA pairs have been reported for II–VI compounds. Thus the effective mass approximation ordinarily used seems to be insufficient in the case of deep centres in II–VI compounds. The second problem arises from the fact that there is not such direct evidence of the existence of recombination in closely associated DA pairs of deep centres in II–VI compounds as has been found in III–V compounds. The strong electron–phonon interaction causes the broad Gaussian shape of deep luminescence bands without any structure even at very low temperatures. This is why the discrete lines corresponding to different separations between donors and acceptors may be masked. The third problem is connected with the relation between free-to-bound and bound-to-bound recombination. It is known that the free electron may recombine with the hole bound to the DA complex. In this case the radiative recombination occurs also at high temperatures. Moreover, the screening of the hole by surrounding defects may cause phenomena, which are typical for bound-to-bound recombination such as *j*-shift or *t*-shift [10, 11]. All these facts indicate the need for further investigations of DA complexes in II–VI materials, primarily by new methods.

In this paper we will try to show that the analysis of the effect of preparation conditions on the shape of the deep luminescence bands, as has been done for the green edge emission band of CdS in [17], may be useful in understanding the DA recombination in II–VI materials.

Orange luminescence (O-band) in silver doped CdS is a typical representative of the deep luminescence band in II–VI materials. At 77 K it has an almost perfect Gaussian shape with  $E_{\max} = 2.0$  eV and half-width  $W = 0.25$  eV. But many authors have discovered the alteration of these parameters of the O-band with changing preparation conditions [4, 6–8]. Unfortunately, most of the authors have not pursued complex and systematic investigations into the effect of preparation conditions on the shape of the O-band. In our previous paper the chemical nature of the O-centre in CdS:Ag:Cl was determined using the quasichemical analysis of luminescence intensity [12]. It was shown that the  $Ag_{Cd}Ag_i$  complex is connected with the O-band. The same complex was also found by Rizakhanov *et al.* [4] to be responsible for the O-band in CdS:Ag crystals and besides, at 77 K the bound-to-bound recombination with  $R_i > 15$  Å occurs. According to the theory of statistical distribution of DA pairs proposed by Reiss [13] the distribution functions in general have two maxima for associated and distant pairs, respectively. So in favorable conditions (low concentration of DA pairs, rather deep levels of isolated donors and acceptors, intermediate firing temperatures) we may also expect the appearance of two different luminescence bands. Unfortunately, the preceding analysis showed that, in case of broad luminescence bands, the distance between the bands is not sufficient

to permit the observation of two separate bands. The only phenomenon we can see is the broad luminescence band with variable half-width, peak-positions and symmetry. The detecting and analysis of these variations of the O-band parameters in CdS:Ag:Cl is the purpose of the present paper.

## 2. EXPERIMENTS AND RESULTS

The initial material used was CdS powder containing metallic impurities at the following concentrations: aluminium— $4 \times 10^{15} \text{ cm}^{-3}$ ; copper— $2 \times 10^{15} \text{ cm}^{-3}$ ; silver— $2 \times 10^{15} \text{ cm}^{-3}$ . The oxygen content was  $1.2 \times 10^{18} \text{ cm}^{-3}$ , and the chlorine concentration was not known. The starting powder was purified from chlorine and oxygen for 8 h in  $\text{H}_2\text{S}$  flow at  $800^\circ\text{C}$ . Silver acquired from  $\text{AgNO}_3$  aqueous solution was added to CdS under conditions analogous to the aforementioned purification. Chlorine acquired from  $\text{CdCl}_2$  aqueous solution was added to CdS in evacuated and wedged-up quartz ampoules at  $1050^\circ\text{C}$  for 24 h. The silver content in the samples was determined by the atom absorption method and the chlorine content by potentiometric titration with an accuracy of 5%. The concentration of added impurities was about an order of magnitude or more larger than the concentration of the residual impurities so that any noticeable effect of these impurities was not detected.

The photoluminescence emission spectra measurements were taken using the standard apparatus described in [12]. The luminescence was excited with monochromatic u.v. light ( $\lambda = 365 \text{ nm}$ ) from a 250 W high-pressure mercury lamp. The excitation intensity was estimated to be  $10^{15} \text{ photons cm}^{-2} \text{ s}$  and was kept constant during the whole experiment.

The computer analysis of the measured spectra was carried out to determine the intensity, half-width

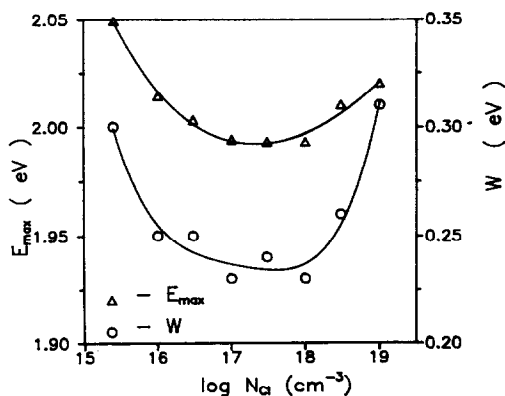


Fig. 1. The dependence of the peak-position and the half-width of the O-band in CdS:Ag:Cl on the chlorine concentration ( $N_{\text{Ag}} = 3 \times 10^{17} \text{ cm}^{-3}$ ).

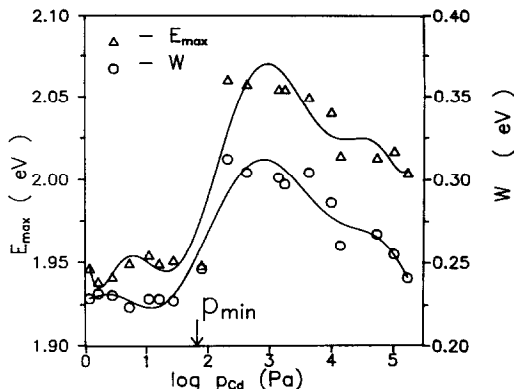


Fig. 2. The dependence of the peak-position and the half-width of the O-band in CdS:Ag:Cl on the partial vapour pressure of the components.

and peak-position of the O-band. It was difficult to observe the small deviation of the O-band from the Gaussian shape because of neighboring G- and R-bands, covered both the high and low energy sides of the O-band. So we considered the shape of the O-band to be the exact Gaussian. This assumption did not affect essentially our results. All the experiments were carried out at 77 K.

The first series of samples was prepared to examine the dependence of the O-band parameters as a function of chlorine concentration. The concentration of silver in all these samples was  $3 \times 10^{17} \text{ cm}^{-3}$  and all the samples were heat-treated at 1120 K under minimum component vapour pressures. After the high-temperature firing treatment the powder samples were rapidly cooled to room temperature to freeze in the thermodynamic equilibrium.

In Fig. 1 the dependence of the peak-position and half-width of the O-band on the concentration of chlorine are presented. As it can be seen from Fig. 1 the minimum for both parameters appear at  $N_{\text{Cl}} = N_{\text{Ag}}$  and the dependencies are similar. The same

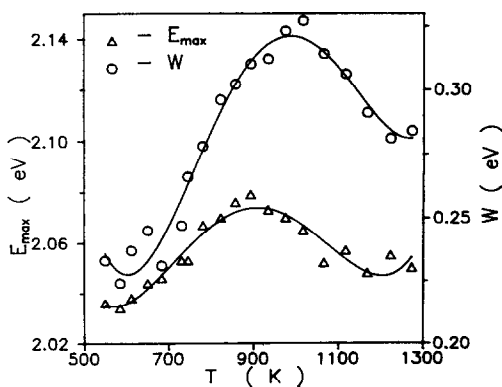


Fig. 3. The dependence of the peak-position and the half-width of O-band in CdS:Ag:Cl on the firing temperature ( $N_{\text{Ag}} = 3 \times 10^{19} \text{ cm}^{-3}$ ,  $N_{\text{Cl}} = 5 \times 10^{15} \text{ cm}^{-3}$ ).

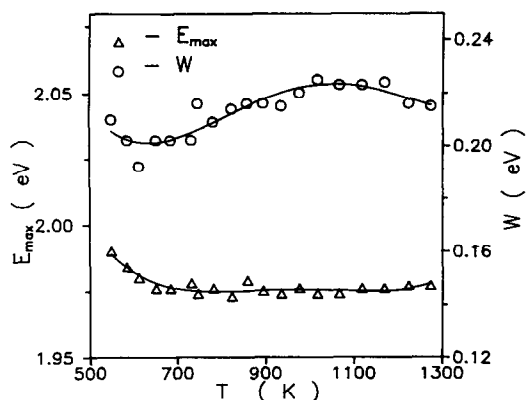


Fig. 4. The dependence of the peak-position and the half-width of O-band in CdS:Ag:Cl on the firing temperature ( $N_{Ag} = 3 \times 10^{17} \text{ cm}^{-3}$ ,  $N_{Cl} = 10^{18} \text{ cm}^{-3}$ ).

similarity can be found in Fig. 2, where the dependencies on the partial vapour pressure of Cd and  $S_2$  are shown. It is known that the partial pressures of the components in CdS are related by the mass action law:

$$K_p = p_{Cd} p_{S_2}^{1/2}, \quad (1)$$

where the reaction constant  $K_p$  for  $T = 1120 \text{ K}$  has been found in [14]. Therefore, only  $p_{Cd}$  is presented in Fig. 2 and  $p_{min}$  separates the partial pressures of cadmium and sulphur. The minimum values for the peak-position and half-width can be found at low  $p_{Cd}$  (i.e. high  $p_S$ ). Radical changes in the parameters of the O-band occur if the  $p_{min}$  point is exceeded. At high  $p_{Cd}$  a new decrease of the parameters occurs.

The third series was prepared to examine the effect of different treatment temperatures on the parameters of the O-band. Two materials were used with  $N_{Ag} = 10^{18} \text{ cm}^{-3}$ ,  $N_{Cl} = 5 \times 10^{15} \text{ cm}^{-3}$  and  $N_{Ag} = 3 \times 10^{17} \text{ cm}^{-3}$ ,  $N_{Cl} = 10^{18} \text{ cm}^{-3}$ , respectively. The treatment temperatures were varied from 1270 K to 550 K and the durations from 4 h to 120 h. All the treatments were carried out under minimum vapour pressure of the components. As can be seen from Fig. 3, the maximum value of the peak-position occurs at 890 K for the material with  $N_{Ag} \gg N_{Cl}$ . At the same time there is no essential change in the parameters of the O-band if  $N_{Ag} = N_{Cl}$  (see Fig. 4).

### 3. DISCUSSION

The generally accepted DA pair distribution function  $G(R)$  was proposed by Reiss [13]:

$$G(R) = CR^2 \exp\left(\frac{q_1 q_2}{\epsilon k T R}\right) \exp\left(-\frac{4}{3} \pi N R^3\right), \quad (2)$$

where  $C$  is a normalization constant,  $R$  is the distance between donor and acceptor in thermodynamic equilibrium produced at temperature  $T$  and  $N$  is the concentration of DA pairs. The distribution function (2) has two maxima and a minimum at:

$$R_c = \frac{q_1 q_2}{2\epsilon k T}. \quad (3)$$

The first maximum will be found at:

$$R = R_0, \quad (4)$$

where  $R_0$  is the shortest distance which can be assumed by a DA pair of the particular kind in the crystal. The second maximum corresponds to distant pairs and lies at:

$$R_m = (2\pi N)^{-1/3}. \quad (5)$$

For a DA pair separated by a distance  $R$ , the emission peak energy ( $E$ ) is given by

$$E = E_g - (E_A + E_D) + \frac{e^2}{\epsilon R}. \quad (6)$$

Maximum and minimum values of the O-band peak-positions can be found from Figs 1 to 4:  $E_{max} = 2.08 \text{ eV}$ ,  $E_{min} = 1.94 \text{ eV}$ . Let us presume these values to be the peak-positions for pure associated and distant DA pairs, respectively. All the other intermediate values of the peak-positions may be treated then as a result of superposition of both maxima. The same situation for half-widths is in force. It is known that the half-width of the associated DA pair luminescence always exceeds the half-width of distant DA pair luminescence because of Coulombic broadening. As can be seen from Figs 1–3, the shift of the O-band peak-position to higher energies is indeed accompanied by a broadening of the same band.

It is obvious that associated DA pairs may exist if

$$R < R_c. \quad (7)$$

From eqn (7) we may conclude that if there are associated DA pairs, then at high temperatures they must be transformed to distant DA pairs with the peak shifting to lower energies and a narrowing of the O-band. This is what we may observe in Fig. 3. The critical temperature  $T = 890 \text{ K}$  according to eqns (7) and (3) gives us a distance for associated DA pairs of  $R = 10.1 \text{ \AA}$  ( $\epsilon = 9.3$  [15]). The Coulombic energy for this distance is  $E = 0.153 \text{ eV}$ . Thus for the distant

DA pairs we obtain an energy of  $E = 0.153 - (2.08 - 1.94) = 0.013$  eV and a distance 119 Å. From eqn (5) we may calculate the corresponding concentration,  $N$ , for distant DA pairs, which turns out to be  $N = 9.4 \times 10^{16} \text{ cm}^{-3}$ . If the concentration of distant DA pairs exceeds the concentration of associated DA pairs, then there is no noticeable alteration of the O-band parameters with temperature (see Fig. 4). In this case only the dependence of  $N$  on  $T$  will cause slight changes. The increasing values of the O-band parameters with temperature if  $T < 890$  K (see Fig. 3) may be explained by the increasing concentration of associated DA pairs with temperature, because at the same time the intensity of the O-band also increased.

The most remarkable changes of the O-band parameters are found in Fig. 2. It is known that the firing of CdS under fixed vapour pressure of the components is a comfortable way to change the Fermi level position without changing total impurity concentration. The transformation of the Fermi level position in turn causes a recharging of the defects and hence affects the Coulombic interaction between donors and acceptors. From Fig. 2 we may conclude that firing in excess sulphur ( $p_{\text{Cd}} < p_{\text{min}}$ ) gives rise to conditions which favor distant DA pairs. This is possible if the Fermi level lies below an isolated acceptor level causing the neutralization of the acceptor and, as a result, a decrease of the Coulomb energy. The same situation is valid at high  $p_{\text{Cd}}$ , where a neutralization of donor defects occurs. Therefore, only at middle values of  $p_{\text{Cd}}$ , where the Fermi level lies between the donor and acceptor levels is strong pairing in force. From Fig. 2 we may also conclude that at high  $p_{\text{Cd}}$  the pure random distribution of DA pairs is not achieved. A possible reason for this is that the donor levels have a certain energetic distribution and the high Fermi level position does not neutralize all the  $\text{Ag}_i$  defects. The strong pairing at the middle values of  $p_{\text{Cd}}$  was also found in CdTe [16].

As can be seen from Fig. 1 increasing the chlorine concentration also affects the O-band parameters although the concentration of O-centres is unchanged [12]. Therefore we may expect the possible influence of chlorine related defects on the coulombic interaction between  $\text{Ag}_i^+$  and  $\text{Ag}'_{\text{Cd}}$ . First of all the charged  $\text{Cl}_s^+$  defects may screen the  $\text{Ag}'_{\text{Cd}}$  acceptors causing a relative decrease of the associated DA pairs concentration. This is what we see in Fig. 1, when  $N_{\text{Cl}} < N_{\text{ag}}$ .

If  $N_{\text{Cl}}$  reaches  $N_{\text{Ag}}$  radical changes in the defect structure occur and most of the charged  $\text{Cl}_s^+$  defects are captured by  $V'_{\text{Cd}}(\text{Cl}_s^+)_2$  complexes [12]. As a result the screening potential decreases and the relative concentration of associated DA pairs increases.

#### 4. CONCLUSION

It has been shown above that the investigation of the shape of broad luminescence bands as a function of preparation conditions of the material can be a sensitive method for detecting the spatial distribution of DA pairs. For the particular case of the O-band in CdS:Ag:Cl our investigations suggest that there are two maxima for associated and random DA pairs, respectively, and most of the observed phenomena can be explained as a result of the superposition of these maxima.

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