

FORMATION OF IMPURITY CLUSTERS IN CdS:Ag:Cl

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Abstract—The Kröger–Brouwer-type analysis of integral intensities of R- and O-luminescence emission bands as a function of the reciprocal temperature of the previous thermal treatment of powder samples under well-defined component vapour conditions has been used for the determination of the enthalpies of impurity cluster formation reactions in CdS:Ag:Cl. The following enthalpies were found

$$2 \text{Ag}'_{\text{Cd}}\text{Cl}'_s = (\text{Ag}'_{\text{Cd}}\text{Cl}'_s)_2 - (0.10 \pm 0.02) \text{ eV},$$

$$2 \text{Ag}'_{\text{Cd}}\text{Ag}'_i = (\text{Ag}'_{\text{Cd}}\text{Ag}'_i)_2 - (0.22 \pm 0.06) \text{ eV}.$$

Keywords: Point defects, CdS, photoluminescence, quasichemical reactions, clusters.

1. INTRODUCTION

An analysis of the defect structure of $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ compounds given in [1–3] indicates that impurity clusters, containing at least three or more point defects, are often the dominating impurity defects in these compounds. Even at high temperatures, where association of point defects usually becomes improbable, the concentration of cluster in powder samples seems to be very high. Unfortunately very little is known about the quasichemical process of association leading to the formation of clusters. In [4] a new method of the quasichemical analysis of defect formation reactions in CdS:Cu:Cl has been proposed. This method is based on a Kröger–Brouwer-type analysis of the luminescence emission curves as a function of the reciprocal temperature of previous thermal treatment of samples under well-defined component vapour conditions. As a result, the enthalpies of some copper cluster formation reactions were found. The purpose of the present paper is to study impurity cluster formation in CdS:Ag:Cl using the same method.

2. EXPERIMENTAL

CdS powders purified and doped with silver ($N_{\text{Ag}} = 3 \times 10^{18} \text{ cm}^{-3}$) and chlorine ($N_{\text{Cl}} = 3 \times 10^{17} \text{ cm}^{-3}$) were fired in an evacuated quartz ampoule under minimum component vapour pressures. The firing time was chosen to be sufficient to reach thermodynamic equilibrium. The detailed description of the purification and doping processes are given in [1]. After the high-temperature firing treatment, the powder samples were rapidly cooled to room

temperature. The photoluminescence (PL) measurements were performed at 77 K with the aid of the standard apparatus also described in (1). In our previous paper the chemical nature of radiative and nonradiative recombination centres in CdS:Ag:Cl has been studied [1]. It was found that the most important deep PL bands, i.e. the O-band, centered at $h\nu = 2.0 \text{ eV}$ and the R-band, centered at $h\nu = 1.7 \text{ eV}$ are due to donor–acceptor complexes $\text{Ag}_{\text{Cd}}\text{Ag}_i$ and $\text{Ag}_{\text{Cd}}\text{Cl}_s$, respectively. In the present paper, the integral intensities Φ of the O- and R-emission bands were determined using a modified Gaussian analysis. The intensity dependence of the PL emission bands Φ_i ($i = \text{O}, \text{R}$) on the firing temperature are shown in Fig. 1.

3. DISCUSSION

In [1] the following expression for the integral intensity of i -PL band Φ_i was given:

$$\Phi_i \sim N_i/N_s, \quad (1)$$

where N_i is the concentration of the radiative recombination centres and N_s the concentration of the nonradiative s-centres. In Brouwer's approximation method, the concentration of a certain point defect [X] in CdS:Ag:Cl is expressed in a certain Brouwer region as [5]

$$[X] = \prod_j K_j^{r_j} N_{\text{Cl}}^a N_{\text{Ag}}^b p_{\text{Cd}}^c, \quad (2)$$

where

$$K_j = K_p \exp\left(-\frac{H_j}{kT_0}\right), \quad (3)$$

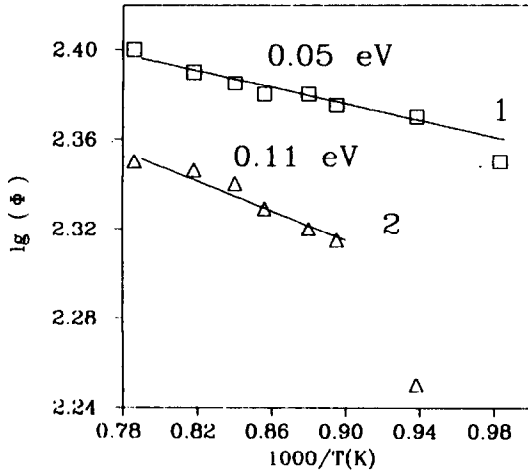


Fig. 1. The dependence of PL emission bands intensity upon the firing temperature in CdS:Ag:Cl. (1) R-band, (2) O-band.

α , β and γ denote the quasichemical coefficients of the X-type defect, H_j the enthalpy of the j -quasichemical reaction, T_0 the firing temperature. Taking into consideration the temperature dependence of the minimum compound vapour pressure one obtains from (2) and (3);

$$[X] \sim N_{\text{Cl}}^{\alpha} N_{\text{Ag}}^{\beta} p_{\text{Cd}}^{\gamma} \exp\left(-\frac{\Delta H}{kT_0}\right) \exp\left(-\frac{2\gamma \Delta H_{\text{CdS}}}{3kT_0}\right), \quad (4)$$

where ΔH is the algebraic sum of the enthalpies of the quasichemical defect formation reactions taking part in the formation of the X-type defect and ΔH_{CdS} is the dissociation enthalpy of CdS. From (1) and (4) we obtain;

$$\phi_i \sim \exp\left(-\frac{\Delta H_i - \Delta H_s}{kT_0}\right) \times \exp\left[-\frac{2(\gamma_i - \gamma_s) \Delta H_{\text{CdS}}}{3kT_0}\right]. \quad (5)$$

This means that, for a certain Brouwer region in co-ordinates $\log \phi_i \sim f(10^3 T^{-1})$ we get the straight line with slope;

$$\phi_i = -\frac{\Delta H_i}{10^3 k \ln(10)}, \quad (6)$$

where

$$\Delta H_i = \Delta H_i - \Delta H_s + \frac{2}{3}(\gamma_i - \gamma_s) \Delta H_{\text{CdS}}. \quad (7)$$

In [1] the defect structure of CdS:Ag:Cl, quenched from 850°C was established. If $N_{\text{Ag}} > N_{\text{Cl}}$, the

following electroneutrality condition and material balance approximations hold

$$[\text{Ag}'_{\text{Cd}}] = [\text{Ag}'_i], \quad (8)$$

$$N_{\text{Ag}} = 4[(\text{Ag}'_{\text{Cd}} \text{Ag}'_i)_2], \quad (9)$$

$$N_{\text{Cl}} = 2[(\text{Ag}'_{\text{Cd}} \text{Cl}'_s)_2]. \quad (10)$$

The chemical nature of the s-centre in this region was also established as $(\text{Ag}'_{\text{Cd}} \text{Ag}'_i)_2$. From eqn (9) we may conclude that;

$$N_s = \text{const.} \quad (11)$$

As it was shown in [1] the Brouwer region in question is characterized by $\gamma_i = 0$ ($i = \text{O}, \text{R}, \text{s}$). Taking into consideration also (11), one obtains from (5)

$$\phi_i \sim \exp\left(-\frac{\Delta H_i}{kT_0}\right). \quad (12)$$

The expressions of ΔH_i for the O- and R-centres we obtain by solving the system of equations, containing the mass action relations (Table 1), the electroneutrality condition (8) and the equations of material balance approximations (9) and (10). The solutions for the temperature range 1017–1272 K, where eqns (8)–(10) are valid, are shown in Table 2.

For the O- and R-bands from Table 2 we obtain;

$$\phi_{\text{O}} \sim [\text{Ag}'_{\text{Cd}} \text{Ag}'_i] = 2^{-1} K_{15}^{-1/2} N_{\text{Ag}}^{1/2}, \quad (13)$$

$$\phi_{\text{R}} \sim [\text{Ag}'_{\text{Cd}} \text{Cl}'_s] = 2^{-1/2} K_{11}^{-1/2} N_{\text{Cl}}^{1/2}. \quad (14)$$

Taking into consideration (3), (7) and (12) and Fig. 1, one obtains, from (13) and (14);

$$\Delta H_{\text{O}} = 0.11 \pm 0.03 \text{ eV} = -1/2 H_{15}, \quad (15)$$

$$\Delta H_{\text{R}} = 0.05 \pm 0.01 \text{ eV} = -1/2 H_{11}. \quad (16)$$

Table 1. Mass action relations for CdS:Ag:Cl

K_1	$= [\text{V}_s^{\bullet\bullet}] n^2 p_{\text{Cd}}^{-1}$
K_2	$= [\text{V}_s^{\bullet\bullet}] [\text{V}_{\text{Cd}}^{\bullet\bullet}]$
K_3	$= [\text{V}_s^{\bullet\bullet}] n [\text{V}_s^{\bullet}]^{-1}$
K_4	$= [\text{V}_{\text{Cd}}^{\bullet\bullet}] n [\text{V}_{\text{Cd}}^{\bullet}]^{-1}$
K_5	$= [\text{S}_{\text{Cd}}^{\bullet}] n p_{\text{Cd}}^2$
K_6	$= [\text{V}_{\text{Cd}}^{\bullet\bullet} \text{Cl}'_s] [\text{Cl}'_s]^{-1} [\text{V}_{\text{Cd}}^{\bullet}]^{-1}$
K_7	$= [\text{V}_{\text{Cd}}^{\bullet\bullet} (\text{Cl}'_s)_2] [\text{Cl}'_s]^{-1} [\text{V}_{\text{Cd}}^{\bullet} \text{Cl}'_s]^{-1}$
K_8	$= [\text{V}_{\text{Cd}}^{\bullet\bullet}] [\text{Ag}'_i] [\text{Ag}'_{\text{Cd}}]^{-1}$
K_9	$= [(\text{Ag}'_{\text{Cd}})_2] [\text{Ag}'_{\text{Cd}}]^{-2}$
K_{10}	$= [\text{Ag}'_{\text{Cd}} \text{Cl}'_s] [\text{Ag}'_{\text{Cd}}]^{-1} [\text{Cl}'_s]^{-1}$
K_{11}	$= [(\text{Ag}'_{\text{Cd}} \text{Cl}'_s)_2] [\text{Ag}'_{\text{Cd}} \text{Cl}'_s]^{-2}$
K_{12}	$= [(\text{Ag}'_{\text{Cd}} \text{S}_{\text{Cd}})'] n^{-1} [\text{Ag}'_i]^{-1} [\text{V}_{\text{Cd}}^{\bullet}]^{-1} [\text{S}_{\text{Cd}}^{\bullet}]^{-1}$
K_{13}	$= [\text{Ag}'_{\text{Cd}} \text{V}_s] [\text{Ag}'_{\text{Cd}}]^{-1} [\text{V}_s^{\bullet}]^{-1}$
K_{14}	$= [\text{Ag}'_{\text{Cd}} \text{Ag}'_i] [\text{Ag}'_{\text{Cd}}]^{-1} [\text{Ag}'_i]^{-1}$
K_{15}	$= [(\text{Ag}'_{\text{Cd}} \text{Ag}'_i)_2] [\text{Ag}'_{\text{Cd}} \text{Ag}'_i]^{-2}$

Table 2. Defect concentration expressions for CdS:Ag:Cl

Defect	Expression for defect concentration
V_S^*	$K_2 K_8^{-1}$
V_{Cd}''	K_8
V_{Cd}'	$K_1^{1/2} K_2^{1/2} K_3^{-1} K_8^{-1/2} p_{Cd}^{1/2}$
n	$K_1^{-1/2} K_2^{1/2} K_4 K_8^{1/2} p_{Cd}^{-1/2}$
V_S^*	$K_1^{1/2} K_2^{-1/2} K_8^{1/2} p_{Cd}^{1/2}$
S_{Cd}'	$K_1^{-1/2} K_2^{1/2} K_3 K_8^{1/2} p_{Cd}^{-3/2}$
Cl_S^*	$K_{10}^{-1} K_{11}^{-1/2} K_{14}^{1/2} K_{15}^{1/4} N_{Cl}^{1/2} N_{Ag}^{-1/4}$
$V_{Cd} Cl_S^*$	$K_6 K_8 K_{10}^{-1} K_{11}^{-1/2} K_{14}^{1/2} K_{15}^{1/4} N_{Cl}^{1/2} N_{Ag}^{-1/4}$
$V_{Cd} (Cl_S^*)_2$	$K_6 K_7 K_8 K_{10}^{-1} K_{11}^{-1/2} K_{14}^{1/2} K_{15}^{1/4} N_{Cl} N_{Ag}^{-1/2}$
Ag_{Cd}'	$2^{-1/2} K_{14}^{-1/2} K_{15}^{-1/4} N_{Ag}$
Ag_i^*	$2^{-1/2} K_{14}^{-1/2} K_{15}^{-1/4} N_{Ag}$
$Ag_{Cd}' Ag_i^*$	$2^{-1} K_{15}^{-1/2} N_{Ag}^{1/2}$
$Ag_{Cd}' Cl_S^*$	$2^{-1/2} K_{11}^{-1/2} N_{Cl}^{1/2}$
$(Ag_{Cd}' Cl_S^*)_2$	$2^{-1} N_{Cl}$
$(Ag_{Cd}')_2$	$2^{-1} K_9 K_{14}^{-1} K_{15}^{-1/2} N_{Ag}^{1/2}$
$(Ag_{Cd}' S_{Cd}')'$	$2^{-1/2} K_5 K_8 K_{12} K_{14}^{-1/2} K_{15}^{-1/4} p_{Cd}^{-2}$
$Ag_{Cd}' V_S^*$	$2^{-1/2} K_1^{1/2} K_2^{1/2} K_3^{-1} K_8^{-1/2} K_{13} K_{14}^{-1/2} K_5^{-1/4} N_{Ag}^{1/4} p_{Cd}^{1/2}$
$(Ag_{Cd}' Ag_i^*)$	$N_{Ag} 2^{-2}$

From (15) and (16) we obtain the enthalpies of the following quasichemical defect formation reactions

$$2 Ag_{Cd}' Cl_S^* = (Ag_{Cd}' Cl_S^*)_2 - (0.10 \pm 0.02) \text{ eV}, \quad (17)$$

$$2 Ag_{Cd}' Ag_i^* = (Ag_{Cd}' Ag_i^*)_2 - (0.22 \pm 0.06) \text{ eV}. \quad (18)$$

As we can see from (17) and (18) the concentration of clusters $(Ag_{Cd}' Cl_S^*)_2$ and $(Ag_{Cd}' Ag_i^*)_2$ decreases with increasing the firing temperature, but this decrease is

quite slow. This is why the concentration of these clusters may be considerable at high temperatures. On the other hand the low values of the enthalpies, especially (17) make the ordinary association at high temperatures improbable because of the high thermal energy. But the enthalpy (18) seems to be sufficient to maintain the dominating concentration of clusters $(Ag_{Cd}' Ag_i^*)_2$ in the above-mentioned temperature range. In a powder sample quenched from high temperatures there must be a high density of dislocations and grain boundaries. These disorders commonly act as a collectors of point defects and therefore we may expect a high concentration of clusters. Thus the formation of clusters may be interpreted as a first stage of impurity precipitation from the crystal lattice.

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