High pressure studies of interimpurity (donor–acceptor) luminescence in ZnS and ZnSe phosphors[a]

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The effect of pressure has been measured on the emission peak location, half-width, integrated intensity, and lifetime for a series of ZnS phosphors doped with Cu^+ or Ag^+ with Cl^-, Al^{3+}, In^{3+}, or Ga^{3+} as coactivator, as well as on self-activated (SA) ZnS and on ZnSe:Cu:Cl. The emission peaks shift to higher energy with increasing pressure, but less strongly than does the absorption edge of the host. The peak intensities decrease rapidly with increasing pressure. The intensity changes could be accounted for quantitatively in terms of the donor–acceptor pair model. The shift of the luminescence peak with respect to the absorption edge is attributed to the pressure coefficient of the donor binding energy E_D. The observed intensity changes with pressure could be related directly to changes in E_D.

INTRODUCTION

High pressure studies have been made on a series of ZnS phosphors doped with Cu^+ or Ag^+ with Cl^-, Al^+, Ga^{3+}, and In^{3+} as coactivators. Studies were also made on self-activated ZnS : Cl and on ZnSe : Cu : Cl. The starting material was luminescent grade powder obtained from Research Organic/Inorganic Corp. The methods of sample preparation follow those of Clieren and van Gool[1] and Hoogenstraaten.[2] Although the firing temperatures were below the cubic–hexagonal transformation temperature, there were traces of the wurtzite phase in the materials as prepared. X-ray analysis showed that the material converted irreversibly to the cubic phase by 2 kbar.

The measurements included emission peak location and half-width, integrated intensity, and lifetimes. The high pressure luminescence techniques, pressure calibration, and methods of data treatment have been presented elsewhere.[3] Some data were obtained as a function of temperature at various pressures using a technique developed by Tyner.[4] The lifetime measurements were made on the apparatus developed by Klick.[5] Most of the data were taken in the quasihydrostatic cell using NaCl as a pressure transmitting medium. The changes obtained were reversible. In addition, runs were made to 12 kbar in a cell using hexane as a medium. These results agreed with those obtained in the quasihydrostatic cell over the same pressure range.

Initial investigations of the pressure effect on the emission bands in ZnS phosphors were carried out by Ortman and Treptow.[6] Pressures of 6 kbar were attained. More recent studies by Koda and colleagues[7] have extended this range to 40 kbar. In both of these investigations the spectral location as a function of pressure was determined. The shift of the fundamental absorption edge of ZnS as a function of pressure has not been established on thin crystals by modern techniques over a large range of pressures. Early experiments on thick crystals using a pressure calibration which is now outdated gave a value of approximately 6–6.5×10^{-3} eV/

kbar for ZnS with the shifts for ZnSe and ZnTe some 10%–20% greater in magnitude. Recent calculations by Cohen[8] give for ZnSe a shift of the direct gap of 11×10^{-3} eV/kbar, which agrees closely with the experimental value.[9] Very recent experiments by Weinstein[10] on ZnTe give for the absorption edge

$$E = 2.55 + 0.0115p - 5 \times 10^{-5}p^2 , \tag{1}$$

where E is in eV and p in kbar. Thus, ZnSe and ZnTe agree closely in the linear terms. A reasonable estimate of ZnS would then be 9–10×10^{-3} eV/kbar. Over the range of 1.7 kbar Piper *et al.*[11] obtain experimentally 9×10^{-3} eV/kbar. For the calculations in this work we use the value of 9×10^{-3} eV/kbar for ZnS. An error of up to 10% in this value would result in changes well within the limits of accuracy of some of the other parameters used in the analysis.

There have been a variety of treatments of ZnS phosphors containing these dopants,[12–16] each of which accounts for some aspects of the behavior of these complex phosphors. We have used here the interimpurity or donor–acceptor model first proposed by Prener and Williams.[15] The necessary features are presented in the discussion.

RESULTS

Smoothed experimental data for peak location, half-width, and relative intensity appear in Table I and lifetime data in Table II. We outline the major features exhibited by these measurements in this section, presenting figures only to illustrate specific points or where they are compared with theory later in the paper.

Peak location and half-width

In general, the luminescent peak shifts to higher energy with increasing pressure, but not so rapidly as the absorption edge. This is illustrated in Fig. 1 for ZnS : Cu : Al and in Fig. 2 for ZnSe : Cu : Cl. The results for the other dopants are qualitatively similar except that the shift for the self-activated material is somewhat larger than the others. This is possibly due to the vacancies introduced in preparing self-activated ZnS.

The half-widths either were constant with pressure or

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TABLE I. Measured parameters versus pressure for ZnS and ZnSe phosphors Pressure (kbar).

Compound	0	5	10	15	20	30	40	50	60	70	80
ZnS : Cu : Cl											
$h\nu_e$	18.50	18.75	19.02	19.30	19.60	20.13	20.62	21.04	21.40	21.70	21.94
$\delta E_{1/2}$	3.10	3.085	3.00	3.00	3.00	3.00	3.00	...	...	...	...
I	1.00	0.89	0.73	0.60	0.49	0.29	0.18	0.11	0.073	0.048	0.031
ZnS(SA)Cl											
$h\nu$	21.30	21.70	22.12	22.52	22.41	23.62	23.97	24.26	24.50	24.73	24.93
$\delta E_{1/2}$	3.78	3.73	3.68	3.63	3.60	3.53	3.52	...	...	...	...
I	1.00	0.78	0.66	0.59	0.50	0.34	0.22	0.14	0.078	0.036	0.014
ZnS : Ag : Cl											
$h\nu$	21.50	21.82	22.08	22.38	22.90	23.14	23.60	24.02	24.40	24.74	25.06
$\delta E_{1/2}$	3.10	3.06	3.02	2.98	2.94	2.86	2.78	2.70	2.62	2.50	2.46
I	1.00	0.94	0.92	0.89	0.81	0.64	0.45	0.27	0.14	0.06	0.024
ZnSe : Cu : Al											
$h\nu$	18.50	18.78	19.05	19.39	19.60	20.13	20.13	20.60	21.00	21.34	...
$\delta E_{1/2}$	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	...	...
I	1.00	0.90	0.77	0.64	0.51	0.30	0.17	0.094	0.048	...	...
ZnS : Cu : In											
$h\nu$	18.50	18.72	19.06	19.51[a]	20.16[b]						
$\delta E_{1/2}$	3.10	3.10	3.10	3.10[a]	3.10[b]						
I	1.00	0.60	0.33	0.13[a]	0.042[b]						
ZnS : Cu : Ga											
$h\nu$	18.50	18.68	18.81	19.27[a]	19.91[b]						
$\delta E_{1/2}$	3.40	3.40	3.40	3.40[a]	3.40[b]						
I	1.00	0.74	0.31	0.16[a]	0.047[b]						

$h\nu$ = peak location (10^3 cm^{-1}); $\delta E_{1/2}$ = half-width (10^3 cm^{-1}); I = intensity relative to one atmosphere at room temperature.

[a]16 kbar.   [b]24 kilobars.

decreased. The decrease is especially noticeable for ZnS : Ag : Cl and ZnS(SA)Cl (see Table I).

Intensities

The intensity of the emission peak decreases drastically with increasing pressure, in some cases by almost two orders of magnitude in 80 kbar. Figures 3–5 illustrate these results for ZnS : Cu : Al, ZnS : Cu : Cl, and ZnSe : Cu : Cl, respectively. The solid curves la-

TABLE II. Lifetime versus pressure for several of the donor–acceptor type ZnS phosphors.[a]

	Cu : Cl		Cu : Al		Cu : In	SA	
P	τ_1	τ_2	τ_1	τ_2	τ	τ_1	τ_2
0	32	300	11	109	23	6	50
8	17	185	11	110	22	4.8	41
16	11	98	12	110	21	4.2	36
24	9.7	85	11	105	19	...	...
28	...	...	...	...	...	3.1	37
32	5.3	110	11	110	19	...	...
40	4.1	57	10	102	18	2.6	...

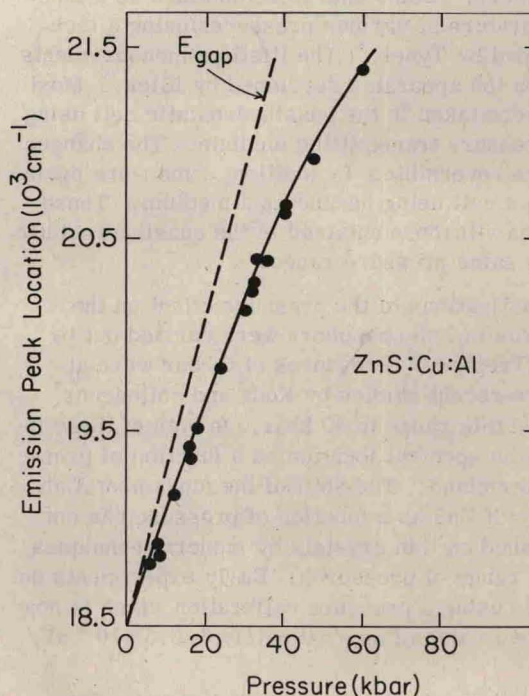[a]All components fit to exponential functions. Time constant τ in msec.

FIG. 1. Emission peak location versus pressure for ZnS : Cu : Al.