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High pressure luminescence studies of mixed ZnS–CdS phosphors doped with Cu^+ or Ag^+ [a)]

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The effect of pressure has been measured on the emission peak location and emission intensity for a series of phosphors of the form $(Zn_xCd_{1-x})S:Ag:Cl$ and $(Zn_xCd_{1-x})S:Cu:Cl$. The results are qualitatively consistent with the donor–acceptor model. The emission peaks shift to higher energy with increasing pressure but the magnitude of the shift decreases with increasing fraction of Cd. The pressure shift of the absorption edge of CdS is also smaller than that for ZnS. The emission peak shift is always less than the shift of the edge for any given fraction of Cd. Large intensity decreases are observed with increasing pressure for each of the phosphors. The observed intensity changes can be related to changes in the donor binding energy with increasing Cd concentration.

INTRODUCTION

The effect of pressure has been measured on a series of mixed crystals of the type $(Zn_xCd_{1-x})S$: Ag and $(Zn_xCd_{1-x})S$: Cu coactivated with Cl. The methods of sample preparation and high pressure luminescence techniques are given in references in the previous paper.[1] The measurements taken include emission peak location and steady state intensity.

ZnS and CdS form a continuous series of solid solutions having the hexagonal wurtzite structure. The lattice constants increase with increasing cadmium concentration and the absorption edge shifts progressively from 3350 Å in ZnS to 5100 Å for CdS. When cadmium is introduced in ZnS phosphors activated with monovalent ions there is a gradual shift of the emission spectra to longer wavelengths as the cadmium content increases. This is a natural consequence of the decrease in band gap; it is known that the position of activator (acceptor) levels remain unaffected upon Cd^{2+} substitution.[2] The replacement of Zn^{2+} by Cd^{2+} results in both a decrease in trap depths (donors) and the appearance of new traps associated with perturbations of Cd^{2+} near the coactivator.[2] Leverenz[3] discusses the influence of the Cd^{2+}/Zn^{2+} ratio on the emission properties of $(Zn_xCd_{1-x})S$ phosphors doped with donor–acceptor type impurities. Several articles are available which cover these materials in greater detail.[2,4–6]

RESULTS

Table I gives the zero pressure peak locations for the mixed crystals studied. The measured peak shift as a function of pressure is shown in Fig. 1 for the $(Zn_xCd_{1-x})S$: Ag phosphor. The mole fraction Zn^{2+} is given by x. Data for the $x=0$ case CdS: Ag could be obtained only up to 25 kbar; at this pressure CdS transformed from the wurtzite to sodium chloride phase.[7] Over the first 40 kbar all the observed shifts appear nearly linear. It is observed that an increase in the Cd^{2+} content is accompanied by a reduction in the linear pressure coefficient. The values obtained for this coefficient are 52, 37, and 25 cm^{-1}/kbar for $x=1.0$, 0.5, and 0, respectively. Figure 2 presents results obtained on the $(Zn_xCd_{1-x})S$: Cu crystal. The linear pressure coefficients are found to be 55, 50, and 39 cm^{-1}/kbar for $x=1.0$, 0.75, and 0.50, respectively. These coefficients compare favorably over a similar range of cadmium concentration with those determined above for the silver-doped system.

Figures 3 and 4 give, respectively, the relative emission intensity versus pressure for the Ag^+ and Cu^+-doped phosphors. In the case of Ag^+ the observed intensity changes with pressure appear to be on two curves, distinctly different, depending on the Cd^{2+} concentration. A different effect is noted in the intensity behavior of the Cu^+ systems. Here is it seen that as the mole percent Zn^{2+} is decreased the intensity at low pressure becomes less sensitive to pressure while the opposite behavior is observed at high pressures.

DISCUSSION

Qualitatively, the behavior of the mixed crystal systems was found to be very similar to the ZnS compounds doped with monovalent cations. The blue shifts and large intensity losses with pressure are seen to be common phenomena, characteristic of the donor–acceptor type emissions studied herein.

The observed emission peak shifts with pressure can be understood when one examines the pressure coefficients of the absorption band edge for pure ZnS (73 cm^{-1}/

TABLE I. Zero pressure peak locations for mixed crystals.

x	$(Zn_xCd_{1-x})S:Ag$ $h\nu_0$(1000 cm^{-1})	$(Zn_xCd_{1-x}):Cu$ $h\nu_0$(1000 cm^{-1})
1.0	21.5	18.5
0.75	...	16.1
0.50	17.0	13.8
0	11.4	...

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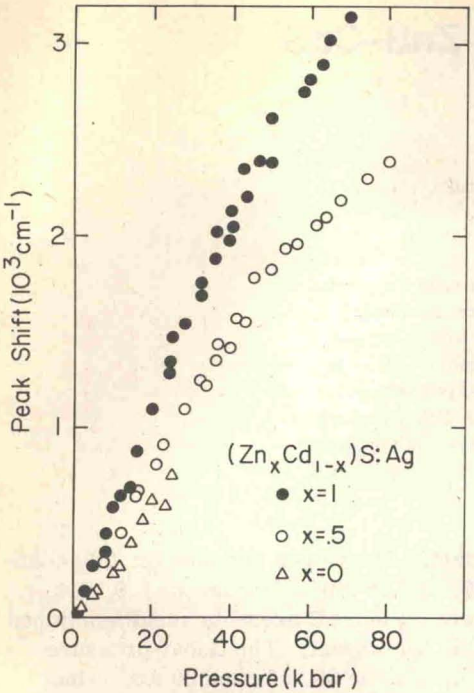

FIG. 1. Emission peak shift versus pressure for $(Zn_xCd_{1-x})S:Ag:Cl$ phosphors.

kbar) and CdS (40 cm^{-1}/kbar). Assuming that a change in the mole percent cadmium results in a linear energy change in the pressure coefficient of the optical band gap the rate of change of this gap (in cm^{-1}/kbar) with

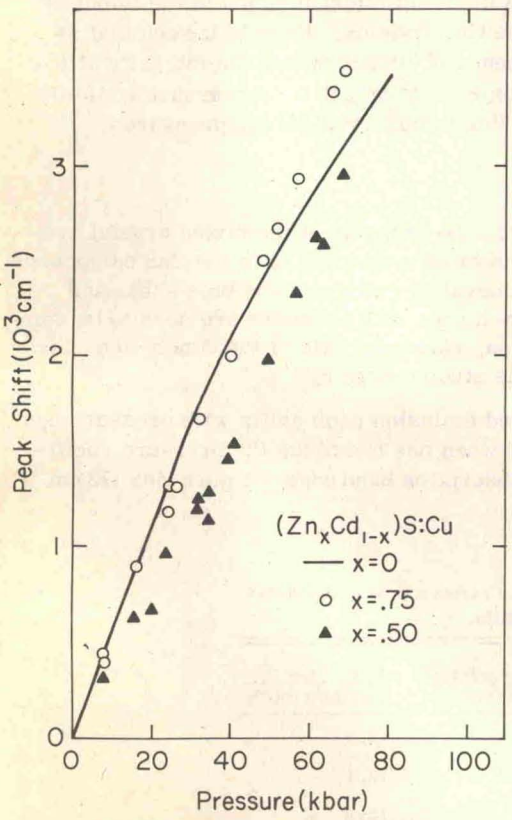

FIG. 2. Emission peak shift versus pressure for $(Zn_xCd_{1-x})S:Cu:Cl$ phosphors.

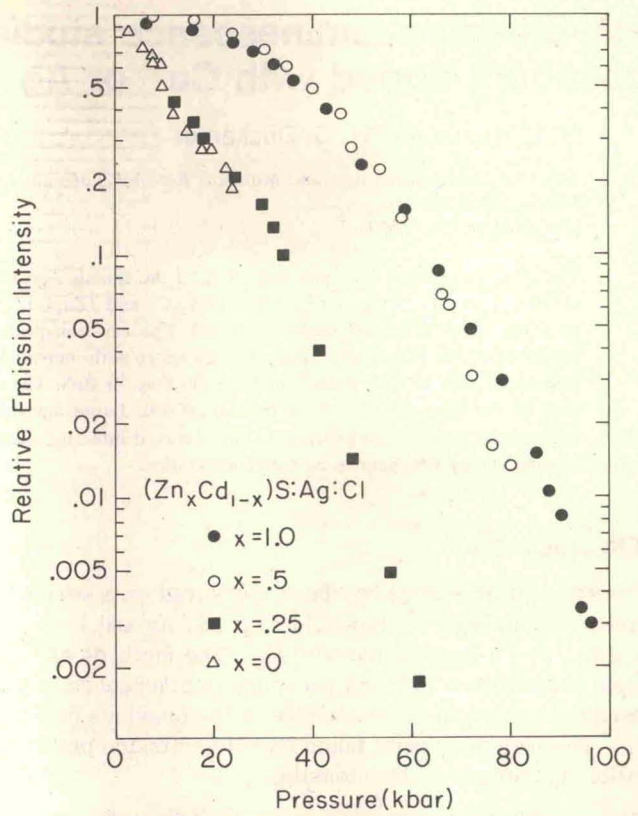

FIG. 3. Relative emission intensities versus pressure for $(Zn_xCd_{1-x})S:Ag:Cl$ phosphors.

pressure for a mixed crystal may be expressed as

$$\frac{dE_g(x)}{dp} = 33(x-1)+73, \tag{1}$$

where x is the mole fraction Zn^{2+}. As observed for the ZnS phosphor doped with Cu^+ and Ag^+ the emission peaks

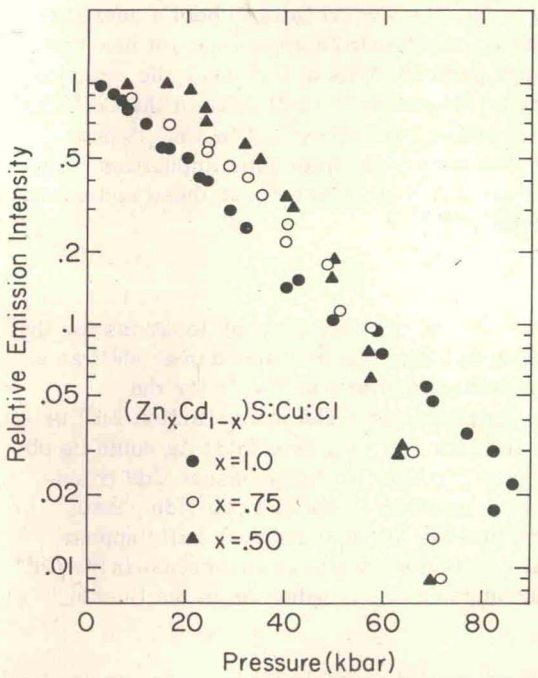

FIG. 4. Relative emission intensities versus pressure for $(Zn_xCd_{1-x})S:Cu:Cl$ phosphors.

of the mixed crystals have pressure coefficients measurably less than the respective band gap. As concluded previously[1] this fact makes it unlikely that the luminescent transition originates directly from the conduction band. Apparently, donor–acceptor luminescence is the dominant mode of radiative recombination.

A qualitative understanding of the observed intensity changes with pressure for the mixed crystals can be achieved through a donor–acceptor model. As has been stated the donor depth becomes shallower as the cadmium concentration is increased. The acceptor level is unaffected. Experimental results presented for the ZnS phosphors have shown the effect of pressure to be to increase the ionization energy of the chlorine donor (~32 cm^{-1}/kbar). Experimental data from Böer *et al.* have indicated that donor ionization energies in CdS increase by roughly 64 cm^{-1}/kbar.[8] These observations make it likely that the donor pressure coefficient in a zinc–cadmium sulfide mixed crystal will be somewhere between these limits. If this is the case, then it is expected that pressure will decrease the emission intensity to a greater extent as the Cd^{2+} concentration is increased. This argument follows from the overlap considerations presented in the previous paper[1] for the ZnS donor–acceptor type emissions. The data for the silver-doped sample at all pressures and the copper-doped sample at pressures greater than 20 kbar bear this out. The anomalous behavior in the copper-doped sample below 20 kbar is not understood.

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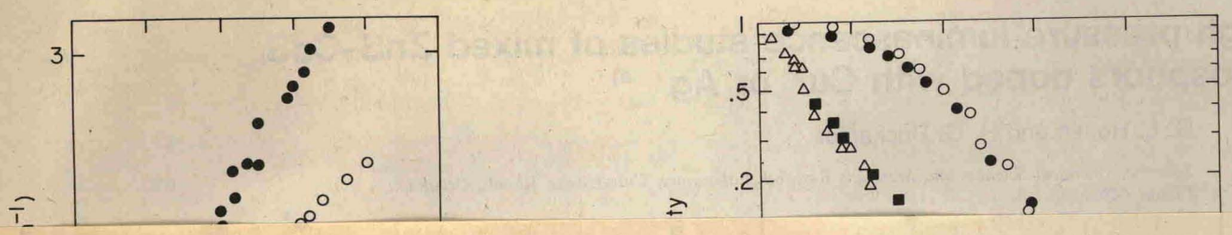
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