JOURNAL OF SOLID STATE CHEMISTRY **106**, 144–149 (1993)

The Effect of Pressure on the Luminescence of ZnS and $Zn_xCd_{1-x}S$ Doped with Cu^+, Cl^-, and Al^{3+}*

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Received December 4, 1992; accepted December 23, 1992

IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

Photoluminescence measurements as a function of pressure were made on ZnS and $Zn_xCd_{1-x}S$ (x = 0.937) samples doped with Cu^+, Cl^-, and Al^{3+}. A limited amount of thermoluminescence and optical absorption data aided in the interpretation. In contrast to the ZnS : Cu : Cl studied earlier, these materials were light yellow in color and could be excited by the 442-nm as well as the 325-nm line of a He–Cd laser. When excited by the 325-nm line into the conduction band the emission peaks shifted to higher energy at a rate which could be related to the increase of the energy gap with pressure. Optical absorption data combined with the excitation spectra of Hoshina and Kawai demonstrated that for the $Zn_xCd_{1-x}S$ phosphor 442-nm excitation was via an exciton band apparently pinned to the conduction band. For ZnS the 442-nm excitation was from a complex acceptor band to the conduction band. The peak shift with pressure indicated that the upper states of this band were no longer pinned to the valence band.

In this study we present high pressure photoluminescence (together with a certain amount of thermoluminescence) data for two II–VI phosphors. A few optical absorption results were also obtained. The phosphors were obtained from the Sylvania Division of GTE and are of technological importance. The analyses are shown in Table I.

We compare their behavior with the results of a previous study on three ZnS : Cu : Cl phosphors (*1*). In the previous study photo and thermoluminescence was observed from three ZnS phosphors doped with Cu^+ and Cl^-. The Cl^-/Cu^+ ratio was ~8 in all phosphors. The sample was excited using the 325-nm (3.82-eV) line of a He–Cd laser. Two emission peaks were observed in photoluminescence one at ~22,000 cm^{-1} (2.73 eV) and one at 20,000 cm^{-1} (2.48 eV). The lower energy (green) peak is associated with a transition from a Cl^- donor to a Cu^+ acceptor. The higher energy blue peak is associated with a transition from a Cl^- donor to a zinc vacancy $[Zn^0Cl]^+$. The green emission shifted to higher energy exactly as the absorption edge (6.4 meV/kbar), which indicates that the Cl^- donor is pinned to the bottom of the conduction band and Cu^+ acceptor is pinned to the top of the valence band. The shift of the blue peak was similar but the Zn vacancy is not quite so closely pinned to the valence band.

The thermoluminescence peaks were measured at two constant heating rates (0.74 K/sec and 0.29 K/sec). For all samples the

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* This work was supported in part by the Division of Materials Science, Department of Energy under Contract DEFG02-91ER 45439.

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0022-4596/93 $5.00

TABLE I

PHOSPHOR COMPOSITION (mole%)

	Cd	Cl	Cu	Al
ZnS	0	0.156%	0.032%	0.094%
$Zn_xCd_{1-x}S$	6.3%	0.13%	0.01%	0.039%

initial trap depth was ~0.27 eV and at first increased with pressure at the same rate as the absorption edge. At higher pressures the trap depth became independent of pressure with a value which was lowest for the sample with highest concentration of impurities. Since the initial energy gap is 3.66 eV and increases with pressure as noted above, beyond ~20–25 kbar the excitation is to "deep levels" initially resonant in energy with the conduction band, but isolated by symmetry and similar considerations.

It should be pointed out that these materials were white in color and could not be excited by the 442-nm (2.81-eV) line of the He–Cd laser.

Experimental Procedure

The photo- and thermoluminescence techniques have been described elsewhere (*1*, *2*). In contrast to the Zn : Cu : Cl samples, these materials were a pale yellow in color and could be excited by the 442-nm (2.81-eV) line of the He–Cd laser as well as by the 325-nm (3.82-eV) line. The high pressure optical absorption methods have also been discussed previously (*3*).

Results

The purpose of this study is two fold: (1) to see the effect of adding Al^{+3} on the emission properties of a ZnS : Cu : Cl phosphor and (2) to see the effect of replacing a relatively modest amount of Zn^{+2} with Cd^{+2}. As can be seen from Table I, the Al^{+3}/Cu^{+} ratio was ~3/1 for both phosphors, and there was an excess of Cl^- in both samples.

The phosphors studied here were a pale yellow in color, rather than white, and in contrast to the ZnS : Cu : Cl phosphors of the previous study they could be excited by both the 442- and 325-nm lines of the He–Cd laser with approximately the same efficiency at ambient pressure. The initial peak locations were ~18,800 cm^{-1} (2.33 eV) for ZnS and ~18,300 cm^{-1} (2.27 eV) for $Zn_xCd_{1-x}S$, independent of the excitation line used. This compares with an emission peak energy of ~20,000 cm^{-1} (2.48 eV) for the green peak of the ZnS : Cu : Cl phosphor studied previously.

In the ZnS phosphor there was only a trace (<5%) of the blue peak observed rather prominently for the ZnS : Cu : Cl phosphor and assigned to emission from Cl^- to a Zn vacancy. No trace of such a peak was observed in the $Zn_xCd_{1-x}S$ material.

When excited by the 325-nm line of the laser both phosphors exhibited a linear shift to higher energy (6.4 meV/kbar for ZnS and 5.4 meV/kbar for $Zn_xCd_{1-x}S$) as shown in Fig. 1. The former shift is exactly the shift of the ZnS absorption edge (*4*), while the latter shift is somewhat less than that of the edge of a phosphor of the given composition (*5*). The intensities decreased with increasing pressure (see Fig. 2) by an amount

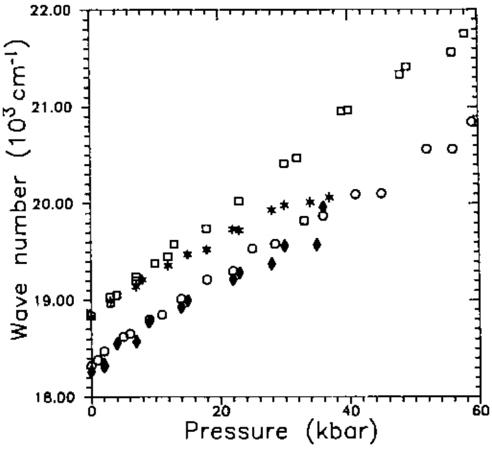

FIG. 1. Peak shift vs pressure. 325-nm excitation: (□) ZnS; (O) $Zn_xCd_{1-x}S$. 442-nm excitation: (*) ZnS; (◆) $Zn_xCd_{1-x}S$.

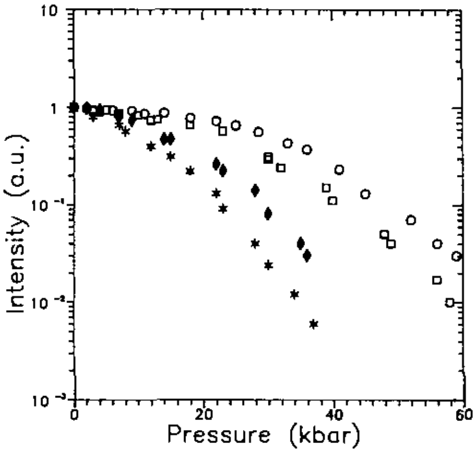

FIG. 2. Peak intensity vs pressure. 355-nm excitation: (□) ZnS; (○) $Zn_xCd_{1-x}S$. 442-nm excitation: (*) ZnS; (◆) $Zn_xCd_{1-x}S$.

closely comparable to that observed for ZnS : Cu : Cl in the previous study.

When the 442-nm line was used for excitation the intensities dropped much more rapidly with pressure than for 325-nm excitation, as shown in Fig. 2. For $Zn_xCd_{1-x}S$ the shift was nearly independent of the excitation line although there was some scatter at high pressure due to the very low intensity. For the ZnS phosphor the initial shift was ~6.4 meV/kbar independent of excitation line, but above ~8–10 kbar there was a continuous decrease in the rate of shift, well beyond experimental error. The thermoluminescence results are exhibited in Table II. For excitation with the 325-nm line the peaks were markedly weaker than those observed for the ZnS : Cu : Cl phosphor of Ref. (*1*), and faded rapidly so data could be obtained for only a few pressures. Within the accuracy of the data the trap depths increased with the increase in the energy gap (perhaps a little more rapidly than the gap for the $Zn_xCd_{1-x}S$ phosphor). The difference in the initial trap depths for the two phosphors ~0.06 eV is the same as the difference in the initial peak location (Fig. 2). For 442-nm excitation data could be obtained only at one atmosphere and only for the $Zn_xCd_{1-x}S$ phosphor. The trap depth was independent of the excitation line used within the accuracy of the measurement.

Atmospheric pressure optical absorption spectra were obtained on both phosphors in the energy range 14,000–29,000 cm^{-1}. For ZnS we observed the low energy tail of a peak almost certainly associated with the exciton peak observed in the excitation spectrum by Hoshina and Kawai (*6*). In addition, there was a broad very low intensity absorption initiating near 21,000 cm^{-1} and extending under the exciton peak, possibly with a maximum near 25,000–26,000 cm^{-1}. This is very probably associated with the broad band in the excitation spectra observed by Hoshina and Kawai (*6*) centered at ~25,000–26,000 cm^{-1}. They associated this band with excitations from a band of acceptor levels to the conduction band. (Similar excitations have been shown to result in photoconductivity (*7*)). The emissions observed when exciting ZnS with the 442-nm laser line was due to excitation in this band.

The absorption spectrum of the $Zn_xCd_{1-x}S$ crystal exhibited a relatively intense absorption with low energy tail extending to ~21,000 cm^{-1} on the low energy side and a broad weak absorption extending to ~17,000 cm^{-1}. The former is almost certainly the exciton peak, and the latter the acceptor to conduction band excitation. For

TABLE II

THERMOLUMINESCENCE RESULTS

Pressure (kbar)		Trap depth (eV)
	325-nm excitation ZnS : Cu : Al : Cl	
0		0.27
9		0.34
	$Zn_xCd_{1-x}S$: Cu : Al : Cl	
0		0.21
9		0.28
17		0.32
	442-nm excitation $Zn_xCd_{1-x}S$: Cu : Al : Cl	
0		0.20

the $Zn_xCd_{1-x}S$ the 442-nm line of the laser excites in the tail of the exciton peak.

It was not possible to obtain any useful high pressure absorption data for ZnS. However, data were obtained for $Zn_xCd_{1-x}S$ to ~40 kbar. The low energy side of the exciton peak (which was all that was observable) shifted to higher energy with increasing pressure at a rate not greatly different from the shift of the absorption edge. There was a significant loss of intensity of the broad absorption at low energy, but the tail still extended to ~17,000 cm^{-1}.

Discussion

Thermoluminescence

We discuss briefly the thermoluminescence results (using excitation at 325 nm). The peaks were weak at one atmosphere and could be followed only over a short pressure range. For the ZnS phosphor the initial value of the trap depth (0.27 eV) corresponds closely to that previously reported (*1*) for ZnS : Cu : Cl. The change with pressure over 9 kbar is ~8 meV/kbar but, given the inaccuracies in the determination of trap depth from weak peaks, it approximates the shift of the absorption edge (6.4 meV/kbar) and corresponds to that observed in the comparable pressure range for ZnS : Cu : Cl. The initial trap depth for the $Zn_xCd_{1-x}S$ phosphor was 0.21 eV. Beliveau and Carlone (*5*) measured the change in location of the absorption edge with composition for a series of $Zn_xCd_{1-x}S$ phosphors, as well as the pressure coefficients of the shifts of edge for various compositions. Interpolation of their date indicate a reduction of the energy gap of ~0.04–0.05 eV for $x \cong 0.94$. This corresponds closely to the difference in trap depth observed here and indicates that the traps are *not* pinned in any way to the bottom of the conduction band, a conclusion which is consistent with the pressure coefficients of the trap depth observed here and in the previous study on ZnS : Cu : Cl. The trap depth increased with pressure at a rate apparently slightly less than that observed for the ZnS phosphor. This would be consistent with the slightly smaller (6.1–6.2 meV/kbar) increase of the energy gap with pressure interpolated from the data of Beliveau and Carlone. In view of the limited accuracy of the data, very little emphasis should be put on this conclusion.

For excitation with the 442-nm line of He–Cd laser the thermoluminescence was very weak, and we could determine only the trap depth for $Zn_xCd_{1-x}S$ at one atmosphere. The value (0.20 eV) corresponds closely to that obtained using the 325-nm line and would indicate that the same traps are involved regardless of the excitation.

Photoluminescence

(*a*) *Excitation with 325-nm (3.82-eV) line.* The results of excitation by the 325-nm line of the He–Cd laser are represented by the squares (ZnS) and circles ($Zn_xCd_{1-x}S$) in Figs. 1 and 2. For ZnS the initial location is 1200 cm^{-1} (0.15 eV) lower in energy than was observed for ZnS : Cu : Cl. In the latter case the donor is Cl^- and the acceptor is Cu^+. For the phosphor studied here the donor may be either Cl^- or Al^{+3}. However, the evidence is (*8–10*) that both donors are located near the conduction band with the Al^{+3} being shallower by ~0.1 eV. Therefore emission from Al^{+3} should be *higher* in energy, assuming the same acceptor. It is very probable that there is a strong tendency for Cu^+ and Al^{+3} to locate in nearby if not adjacent Zn^{+2} sites which could perturb the acceptor energies. (See the discussion in the next section.) The emission shifts to higher energy with pressure at a rate of 6.4 meV/kbar approximately the same as the absorption edge and as the shift observed for ZnS : Cu : Cl. Evidently, in first order, the donors are pinned to the bottom of the conduction band and the acceptors to the top of the valence band.

For $Zn_xCd_{1-x}S$ the initial luminescence energy is ~500 cm^{-1} (0.06 eV) lower in energy than for the ZnS phosphor. This is consistent with the difference in the energy gap (*5*) and of the trap depths as discussed above. There is a linear shift of 5.4 meV/kbar to higher energy with pressure. Ref. (*5*) indicates that the energy gap for a mixed crystal of this composition shifts to higher energy at a rate of 6.1–6.2 meV/kbar. This difference is larger than any experimental error and indicates that the donors and/or acceptors are not as completely pinned to the band edges as for ZnS.

For both phosphors the intensity (area under the emission peak) decreases with increasing pressure at a rate comparable to that observed for the ZnS : Cu : Cl phosphors. The increase in energy of the donor state relative to the acceptor decreases the overlap and allows competing nonradiative pathways to quench the luminescence.

(*b*) *Excitation with 442-nm (2.81-eV) line.* These phosphors are slightly yellow in color and can be excited using the 442-nm line of He–Cd laser. Hoshina and Kawai (*6*) have obtained excitation spectra on ZnS : Cu : Al phosphors (Cl^- content, if any, not given). They show a broad excitation peak centered at ~390 nm (25,600 cm^{-1}) with a half width of 5000–6000 cm^{-1}. This peak is associated with excitation from acceptor levels to the conduction band. Since the Cu^+ acceptor levels in ZnS : Cu : Cl do not exhibit this behavior, this is further evidence for an acceptor center involving Cu^+ and Al^{+3} on nearby sites. It should be mentioned that Berlov *et al.* (*11*) in a theoretical analysis of ZnS doped with Al^{-3} show a center labelled $\overline{Al}$ about 0.8 eV above the top of the valence band which they indicate can provide electron transfer to the conduction band under excitation. They give no physical description of this level. The pressure behavior of the emissions generated by this excitation is interesting. The initial peak locations for both phosphors is identical to that observed for excitation by the 325-nm line. The initial intensities are also similar, but they drop off very rapidly with pressure (see Fig. 2). In the case of this $Zn_xCd_{1-x}S$ material the loss in intensity is due to the shift of the exciton peak to higher energy as the absorption coefficient at 442 nm drops by an order of magnitude. While we have no high pressure absorption data for ZnS, it is reasonable to assume that the broad low energy absorption loses intensity as it does for $Zn_xCd_{1-x}S$ and that this accounts for the loss of emission intensity observed in this material.

The peak energies as a function of pressure are shown in Fig. 1. For the $Zn_xCd_{1-x}S$, the shift is essentially independent of excitation energy although there may be some deviation at higher pressures where the intensity is very low. For ZnS, the initial shift is also the same for the two excitation lines, but above ~10 kbar the rate of shift decreases distinctly with increasing pressure by an amount which is certainly larger than any experimental error. It is relatively straightforward to explain the shift of the emission peak of $Zn_xCd_{1-x}S$. Evidently the exciton peak is essentially pinned to the conduction band and the luminescence process is similar to that when the 325-nm laser line is used except that there is a more rapid drop in intensity with increasing pressure since the availability of states in the tail of the exciton band drops off rapidly as the excitation moves farther out in the tail as the exciton peak shifts to higher energy.

The shift of the emission peak in ZnS with pressure under excitation by 442-nm light is more difficult to explain. The excitation apparently is from sites in the gap to the conduction band. These are probably complex acceptor sites involving interaction between Cu^+ and Al^{+3}. If the pressure behavior of the broad, low energy low intensity band for ZnS is like that for $Zn_xCd_{1-x}S$ the low energy tail of this band does not shift with pressure and thus the states are more nearly tied to the conduction than to the valence band. Emission to these states from the Cl^- donors which are pinned to the conduction band would involve no change in energy with pressure.

Acknowledgment

The authors wish to thank the Sylvania Division of GTE for the samples of two technologically important phosphors. It is a pleasure to acknowledge the support of the Materials Science Division of the Department of Energy Under Contract DEFG02-91ER 45439.

Appreciation

I am delighted to take this opportunity to acknowledge the pioneering work of Professor J. M. Thomas in solid state chemistry. His insight and leadership have done much to establish the field in its present flourishing condition. When I first met Professor Thomas nearly 30 years ago, solid state chemistry was in its infancy as a field with very few practitioners. Professor Thomas has been a key figure in the development of the area. It is my hope that his science and our interactions may continue indefinitely.

H. G. Drickamer

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