

High pressure luminescence studies of localized excitations in ZnS doped with Pb^{2+} and Mn^{2+} a)

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High pressure luminescence measurements have been made on ZnS doped with Pb^{2+} and Mn^{2+} . The data include changes in peak energy and shape, integrated intensities, and lifetimes. These localized emissions are treated in terms of a single configuration coordinate model. For Pb^{2+} the emission peak shifted to lower energy by a moderate amount and narrowed. For excitation in the Pb^{2+} absorption the intensity was independent of pressure, which is consistent with the fact that the energy barrier for radiationless return to the ground state was high at all pressures. For excitation in the ZnS absorption edge the intensity decreased significantly with pressure above about 80 kbar. Data on shifts of the conduction band with pressure would indicate that one is approaching a transition from a direct to indirect transition at high pressure so that decrease in emission intensity may be associated with decreased absorption efficiency. The Mn^{2+} emission peak shifted strongly to lower energy with increasing pressure. The direction and magnitude of the shift were consistent with the predictions of ligand field theory. The intensity doubled in 100 kbar, while the lifetime decreased by roughly a factor of 2. These results could be described in terms of a model for a phonon assisted transition. In addition, peak location, intensity, and lifetime measurements were made on ZnS:Pb:Mn. There is clear evidence of energy transfer by exchange, but in addition there is a nonradiative process in the doubly doped crystal which affects both intensities and lifetimes.

INTRODUCTION

The effect of pressure has been measured on the luminescence of ZnS doped with Pb^{2+} and with Mn^{2+} . The measurements include emission peak location, half-widths and asymmetry, emission intensity and lifetimes. Some measurements were also made on ZnS doped with both Pb^{2+} and Mn^{2+} to study Pb^{2+} to Mn^{2+} energy transfer. The methods of sample preparation, the high pressure luminescence techniques, and methods of data processing are discussed in references given in the first paper of this series.¹

These impurities when introduced into the host lattice occupy zinc sites and require no charge compensation. Whereas the optical properties of those phosphors discussed in the previous papers were largely determined by the host, the luminescence behavior of these materials is strongly dependent on the nature of the impurity ion. Luminescence in these systems involves optical transitions within the electronic levels of the impurity. Excitation can be achieved either through host absorption or direct absorption by the impurity ion. In the latter case the degree of absorption depends on the oscillator strength of the impurity in the tetrahedral environment. The pressure-dependent configuration coordinate model²⁻⁴ provides the basis for the analysis of these deep levels.

RESULTS

Excitation of the ZnS:Pb phosphor was achieved through host lattice absorption (298 nm Hg line) and also by direct excitation of the Pb^{2+} ion (405 nm Hg

line). The absorption process is the $6s^2 \rightarrow 6sp$ electronic transition. A constant excitation rate was assured in the former case since the flat portion of the fundamental absorption always overlapped the exciting line. Direct excitation at 405 nm is believed to involve the $B(^1S_0 \rightarrow ^3P_2)$ and C band ($^1S_0 \rightarrow ^1P_1$) absorptions.⁵ Excitation spectra yielded a fairly broad absorption peak centered at 430 nm which is insensitive to pressure. The resulting green luminescence occurs via the $^3P_2 \rightarrow ^1S_0$ electronic transition. A detailed study and assignment of energy levels of the Pb^{2+} center in cubic zinc sulfide is given by Uehara.⁵

Figure 1 shows data for ZnS:Pb for both the emission peak shift and half-width change with pressure. In contrast to the donor-acceptor type luminescences where the emission bands exhibited a large blue shift with increasing pressure the Pb^{2+} emission band shows a shift to lower energy. A least squares fit of this data gives the following relation for the band shift (in cm^{-1}) as a function of pressure;

$$\Delta(h\nu_e) = -16p + 0.05p^2. \quad (1)$$

The data for the observed half-width change are fit linearly from 20–120 kbar. The half-width data obtained from 0–20 kbar required the resolution of two peaks and probably do not reflect the true bandwidth variation over this pressure range. The additional peak was due to an SA (self-activated) band introduced by chlorine which was present during firing. This band was quenched at pressures greater than 20 kbar. At 20 kbar the Pb^{2+} bandwidth was approximately 0.22 eV. The observed half-width change with pressure obeyed the following relation:

$$(\delta E_{1/2})_e = -5.8p, \quad (2)$$

where $(\delta E_{1/2})_e$ is in cm^{-1} .

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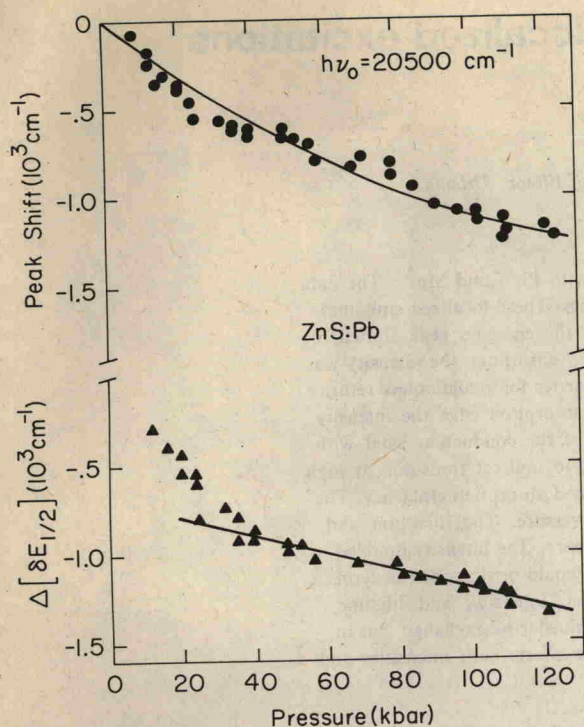


FIG. 1. Emission peak shift and half-width change versus pressure for ZnS:Pb ($\delta E_{1/2}$)₀ = 2390 cm^{-1} by extrapolation of the fit curve to $p=0$.

The band location at 1 atm and the observed peak shift and half-width change were independent of the exciting wavelength. Absorption by the host and direct excitation of Pb^{2+} ion yielded identical results.

Figure 2 gives the steady state intensity and the observed lifetime of the ZnS:Pb phosphor as a function of pressure. In the case of Pb^{2+} excitation there is little change in the intensity over the entire pressure range. Excitation in the fundamental lattice absorption band, however, yields a different effect. Here the intensity stays constant up to about 80 kbar at which point a decline begins. The observed decay function is exponential as would be expected by the first order kinetics predicted for a localized center. The measured lifetime is seen to be independent of exciting wavelength and shows a modest increase in the first 30 kbar before leveling at 250 nsec.

The orange luminescence of ZnS:Mn arises from an optical transition with the Mn^{2+} ion. The Mn^{2+} has a $3d^5$ electron configuration with a spherically symmetric ground state ${}^6\text{S}({}^6\text{A}_1)$ —all spins unpaired. The lowest excited state (one spin paired) of this ion is the ${}^4\text{G}$ excited state band comprised of the ${}^4\text{T}_1$, ${}^4\text{T}_2$, and ${}^4\text{A}_1 + {}^4\text{E}$ excited states. The observed emission occurs from the lowest energy excited state ${}^4\text{T}_1$ to the ${}^6\text{A}_1$ ground state;⁶ the transition is forbidden by spin and parity selection rules. These rules become relaxed through perturbations due to one or a combination of the following sources: crystal field, spin-orbit interaction, exchange coupling of Mn^{2+} pairs, or phonon coupling. In the case of phonon coupling it is the breathing mode about the impurity ion that is responsible for the phonon assis-

tance.⁷ The ground state of the manganese ion in zinc sulfide has been estimated to be anywhere from 3 to 6 eV below the top of the valence band. Klick and Schulman⁸ provide further discussion of the luminescence properties of divalent manganese in solids. Their paper shows the applicability of the configuration coordinate model to this center and also includes causes for band asymmetry.

The data of Fig. 3 show the large pressure shift to lower energy for the ZnS:Mn phosphor. The accompanying half-width dependence over this pressure range appears in the top part of Fig. 4. The bandwidth at 1 atm and room temperature was 0.27 eV. As is known the manganese emission band is asymmetric.⁸ A plot of the pressure dependence of this asymmetry is shown in the lower portion of Fig. 4. It is observed that at about 120 kbar the band assumes a Gaussian distribution [$R \rightarrow 1$ in Eq. (3) below]. It is also interesting to note that in each set of data of Figs. 3 and 4 there is a measurable change in the data at approximately 40 kbar.

The final sets of data on the ZnS:Mn system appear in Fig. 5. Plotted here are the steady state intensity and the observed lifetime(s) as a function of pressure. The emission intensity increases by a factor of 2 over the pressure range studied. The decay function was fit to the sum of two exponentials. The 1 atm, room temperature values of the decay constants were 180 and 650 msec. The 650 msec decay is believed due to the phonon-assisted electronic transition within the manganese ion, while the shorter decay is ascribed to a trapping state.^{7,9} As can be seen the longer decay constant shows a gradual decrease with pressure while the faster one stays approximately constant.

DISCUSSION

The influence of high pressure on the optical properties of localized centers in ZnS:Pb and ZnS:Mn is un-

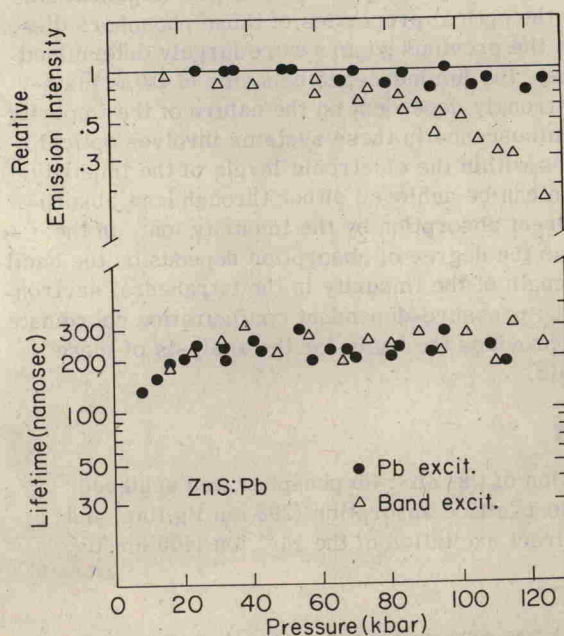


FIG. 2. Relative emission intensity and lifetime versus pressure for ZnS:Pb.