Synopsis

The thesis describes the work carried out by the author during the last three years in the Materials Research Laboratory, Department of Physics, Shivaji University, Kolhapur, on the luminescence studies of \((\text{Zn}:\text{Cd})\text{S}\) phosphors activated with \(\text{Mn}^{2+}\) and coactivated with \(\text{Sm}^{3+}\). The investigation was carried out on the powder samples. Essentially the work described comprises of luminescence studies on \((\text{Zn}:\text{Cd})\text{S}:\text{Mn}:\text{Sm}:\text{Cl}\) phosphors which have not been, to the best of the author’s knowledge, reported so far. EPR studies have also been carried out on some of the samples.

The first chapter is a general introduction giving briefly the present state of knowledge of luminescence and EPR studies on II and VI compounds. This introduction is confined only to the aspects that are intimately related to the present study.

The second chapter gives the details of the experimental techniques followed in the investigation. The basic material used for synthesis of phosphors was prepared by the precipitation method. The phosphors were fired in a silica tubular furnace at 900°C in different atmospheres. The operating characteristics and the excitation sources were different for electroluminescence and photoluminescence studies. For emission spectra three different excitation sources were used. Some of the measurements were carried out at liquid nitrogen and at ambient temperatures. The EPR spectral measurements were carried out on \(X\)-band varian spectrometer and luminescence efficiency was obtained with the help of Nitometer.
The results obtained from the electroluminescence studies are discussed in Chapter-III. The effects of field strength and frequency on EL brightness have been investigated. The voltage dependence of the time averaged electroluminescent brightness shows the relation $B = B_0 \exp \left( -c/\sqrt{V} \right)$ to hold good over a wide range of frequencies, indicating that the mechanism of excitation is acceleration collision. The dependence of constants $B_0$ and $c$ on frequency of the applied field shows that the brightness of EL is saturated at higher frequencies. The EL brightness waveforms are also discussed. From EL spectra it has been observed that for these phosphors the EL peak emissions are at 560 nm and 580 nm.

The fourth chapter describes the results of the fluorescence spectral measurements. The emission spectra are obtained by exciting 365.0 nm, 253.7 nm and by X-rays. The emission spectra obtained by three different excitation sources have been interpreted with the help of ionic crystal bonding and with the familiar Schön-Klasens model for luminescence. The roles of activator, coactivator and of flux are discussed. Due to Mn$^{2+}$ ions in (Zn: Cd)S we are getting emission in the yellow-orange region and with Sm$^{3+}$ ion the emission is found to be in the green region. The (Zn: Cd)S: Mn: Sm: Cl phosphors have emission towards longer wavelengths. The photoluminescence efficiency of these phosphors is directly obtained with the help of Nitometer in nits.

The results obtained from the EPR spectral studies are discussed in Chapter-V. The paramagnetic resonance spectrum of
divalent manganese has been measured for \((\text{Zn}_{x}\text{Cd}_{1-x})\text{S}\) phosphors \((0 \leq x \leq 0.8)\). The spectroscopic splitting factor \(g\) and the hyperfine structure constant \(A\) for some of these phosphors are determined. The parameters of the EPR spectrum and their relations to the other physical properties are discussed. The hyperfine constant for these compounds is found to be between 62 and 73 G. The spectroscopic splitting factor is also found to be about two. The line width varies from 12 to 35 G. The EPR signals due to \(\text{Sm}^{3+}\) ion have not been observed in the employed magnetic field and temperatures.

Chapter-VI is devoted to the discussion of results described in previous chapters. The prominent conclusions of the present study are enumerated as:

1) The electroluminescent brightness and the applied electric field follows the relation

\[ B = B_0 \exp \left( -\frac{c}{\sqrt{V}} \right) \]  

The variation of brightness according to this relation indicates that barriers of Mott-Schottky type are formed in which the thickness of barrier increases as the square root of the applied voltage. The mechanism of excitation is, therefore, an acceleration collision type.

2) The electroluminescent brightness and frequency of applied field follow the relation

\[ B = N_0 f \sqrt{1 - \exp \left( -\frac{A}{f} \right)} \]  

(ii)
3) The brightness waves of the phosphors show only one peak per half cycle of the applied voltage. The brightness waves do not show secondary peaks so that the electron traps are located close to the luminescence centres.

4) From the EL spectral studies it is concluded that Mn\(^{2+}\) and Sm\(^{3+}\) ions in (Zn:Cd)S phosphors have EL emission in nearly the same spectral region. The coactivator affects the spectral emission intensity but not spectral shift in the range studied.

5) The (Zn:Cd)S:Mn:Sm:Cl phosphor emits a reddish yellow luminescence with peak at about 2 eV. The fluorescence emission of the phosphors was explained fully by introducing the traps due to Sm\(^{3+}\) and Mn\(^{2+}\) ions in Schön-Klasens model for luminescence.

6) From EPR studies the parts played by flux, activator and coactivator have been found. For all the phosphors dominant six lines which are characteristic of the hyperfine structure spectrum of manganese were observed.