Journal of Luminescence 40&41 (1988) 700–701
North-Holland, Amsterdam

THE LUMINESCENCE OF MERCURY-LIKE IONS IN ALKALINE EARTH SULFIDES

Zhiran HAO, Yuhua YANG, Xiuhua YIN, Baogui YU and Zhongsu GUAN

Changchun Institute of Physics, Academia Sinica, Changchun, China

The luminescence of mercury-like ions in alkaline earth sulfides is reported, the results show that the luminescence spectra present certain regularity. In CaS two luminescent centers are observed for Pb^{2+} and Bi^{3+} ions respectively. Energy transfer phenomena from mercury-like ions or host lattice to Eu^{2+} in MS are discussed.

1. INTRODUCTION

Mercury-like ions are frequently used in luminescence studies[1-4]. In recent years, there is a growing interest in the luminescence of mercury-like ions in many host lattice. Here we report on the luminescence of mercury-like ions (Ga^+, Ge^{2+}, In^+, Sn^{2+}, Sb^{3+}, Tl^+, Pb^{2+}, Bi^{3+}) and the energy transfer phenomena in alkaline earth sulfides MS(M=Ca, Sr, Ba).

2. EXPERIMENTAL

The experimental techniques were described in Ref. 5.

3. RESULTS AND DISCUSSION

We observed luminescence for the following ions: $Ga^+(4s^2)$, $Ge^{2+}(4s^2)$, $In^+(5s^2)$, $Sn^{2+}(5s^2)$, $Sb^{3+}(5s^2)$, $Tl^+(6s^2)$, $Pb^{2+}(6s^2)$, $Bi^{3+}(6s^2)$, the results with some regularity were obtained. The luminecence of these ions in MS is characterized by the red shift of emission spectra and the broadening of half intensity width with the increase of cation radius of MS. Note that the Stokes shift increases in the sequence of $6S^2$ ions Tl^+, Pb^{2+}, Bi^{3+}, the same is true for $5s^2$ ions In^+, Sn^{2+}, Sb^{3+} and $4s^2$ ions Ga^+, Ge^{2+}. The Stokes shift is smaller for the $5s^2$ ions than for the corresponding $6s^2$ ions, the Stokes shift of $4s^2$ ions is also smaller than that of the corresponding $5s^2$ ions. The luminescence properties are explained in terms of earlier models related to an off-center position of the metal ion. The details of our results will be presented in somewhere else[5].

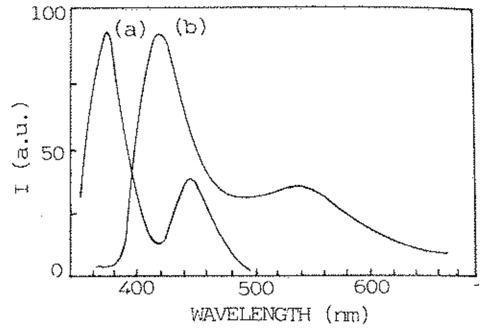

FIGURE 1
Emission spectra of CaS:Bi^{3+}(a) and CaS:Pb^{2+}(b) under 320nm escitation at RT.

In the course of this study we also observed some additional information. The emission band is clear with double peaks for Pb^{2+} and Bi^{3+} in CaS(see Fig. 1), we ascribe the peaks to associated and unassociated luminescence centers. We investigated the energy transfer phenomena from mercury-like ions or host lattice to Eu^{2+} in MS. The peak of Eu^{2+} emission band is near 640nm in CaS. The occurrence of the sensitization of Eu^{2+} can be verified by the measurement of the excitation spectra and the enhancement of Eu^{2+} emission intensity under excitation into Pb^{2+} or the absorption band edge of host lattice(see Fig. 2).

In addition, we also studied the sensitized luminescence of Eu^{2+} by mercury-like ions

0022-2313/88/$03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

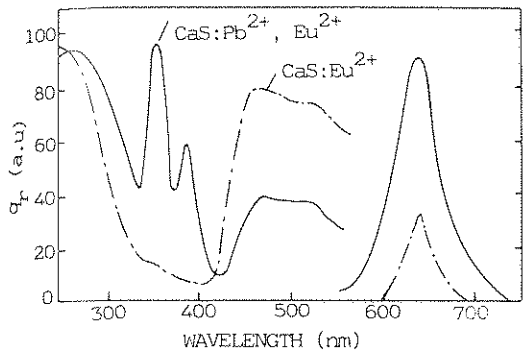

FIGURE 2
Emission spectra and excitation spectra of samples at RT.

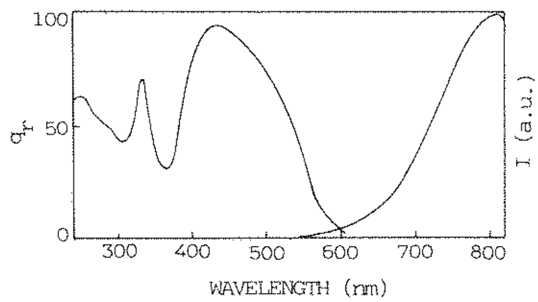

FIGURE 3
Emission and excitation spectra of BaS:Eu^{2+} at RT.

behaving as a sensitized center in BaS. The emission and excitation spectra of Eu^{2+} are given in Fig. 3, the peak of Eu^{2+} emission band is near 810nm. Practically, all samples were found to have a low efficiency for 0.1% Eu^{2+} and 0.1% mercury-like ions, excitation into the mercury-like ions resulted in an emission which consists of about 60% of Eu^{2+} emission and about 40% of mercury-like ion emission. Since the mercury-like ion excitation band overlaps these for Eu^{2+}, the greater part of Eu^{2+} emission observed is probably due to direct excitation into Eu^{2+}. Because energy transfer between mercury-like ions did not take place, we have to evaluate the energy transfer process from the mercury-like ions to Eu^{2+} ioins only by the formula

$$R_c^6 = 0.63X10^{28} Q_A E^{-4} \int f_S(E) f_A(E) dE$$

which expresses the critical distance for electric dipole-dipole interaction. Here Q_A is the absorption cross section of Eu^{2+} ion and E the energy where maximum overlap between mercury--like ions emission and Eu^{2+} ion absorption spectra occur. The integral presents the spectral overlap between emission and absorption. For Q_A we took as an upper maximum $25X10^{-22} cm^2 eV$, the spectra overlap is about $0.02 eV^{-1}$. The result calculated is R_c=3Å.

We consider that due to the large size of Ba^{2+} which prevents Eu^{2+} and mercury-like ion from being close together, therefore the energy transfer has a low efficiency.

REFERENCES

1. C.W.M. Timermans and G. Blasse, J. Solid State Chem., 46 (1982) 222.

2. Hao Zhiran and G. Blasse, J. Solid State Chem. 55 (1984) 55.

3. S. Asano and N. Yamashita, Phys. Stat. Sol. (b), 71 (1980) 311.

4. G. Blasse, Phys. Stat. Sol. (b), 104 (1981) k57.

5. Hao Zhiran, Yang Yuhua, Yin Xiuhua, Yu Baogui and Guan Zhongshu, Chinese J. of Lumin., in print.