Proc. XIX International School of Semiconducting Compounds, Jaszowiec 1990

ON THE NATURE OF Eu-RELATED EMISSIONS IN ZnS AND CaS *

K. ŚWIĄTEK, M. GODLEWSKI

Institute of Physics, Polish Academy of Sciences Al. Lotników 32/46, 02-668 Warszawa,
Poland

L. NIINISTÖ AND M. LESKELÄ

Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo, Finland

(Received August 8, 1990)

The Eu-connected recombination processes in ZnS and CaS are analyzed on the basis of optical studies. A new Eu-related emission in ZnS is attributed to the recombination of an exciton bound at the Eu^{2+} center, while in CaS the emission is dominated by the direct Eu^{2+} intra-ion transition.

PACS numbers: 71.55.Gs, 71.35.+z, 78.55.Et

The studies of Eu activated wide bandgap sulphides are motivated by the possible utilization of these materials in thin film electroluminescence (EL) displays for red colour and after codoping with Ce for white colour [1]. In this paper we present studies of the photoluminescent (PL) properties of ZnS:Eu bulk crystals and CaS:Eu thin films. The crystals and thin films were grown by iodine transport [2] and atomic layer epitaxy [3] methods, respectively.

In principle, europium may enter II-VI compounds in two charge states: Eu^{3+} with a $4f^6(^7F_0)$ electron configuration and Eu^{2+} with a $4f^7(^8S_{7/2})$ configuration of the ground states. The existence of stable Eu^{2+} ions in ZnS and CaS bulk crystals was confirmed by ESR experiments [4-6]. Our photo-ESR studies [4] and theoretical calculations [7, 8] allowed to locate the Eu^{2+} ground state at 2.25 eV below the edge of the conduction band (CB) of ZnS and ~ 2.75 eV in CaS.

The first excited configuration of the Eu^{2+} ion requires excitation of one of the $4f$ electrons to the $5d$ shell. The $4f^n \Rightarrow 4f^{n-1}5d^1$ transition is quite different from the intra-shell $4f^n$ transitions in rare earth (RE) ions. Its energy depends strongly on lattice covalency and the relevant absorption and PL bands are broadened due to the strong electron-phonon coupling of the "external" $5d$ electron. The

*This work was supported by CPBP 01. 12.

Fig. 1. The photoluminescence (left side) and PL excitation (right side) spectra of the CaS:Eu^{2+} thin film measured at 7 and 300 K.

Fig. 2. The energy scheme for Eu^{2+} excitation, ionization, and recombination in ZnS (a) and CaS (b).

crystal field splitting is much larger for the 5d electron than the spin-orbit splitting of the $4f^6$ "core" electrons [9]. An intensive red PL in CaS is related to Eu^{2+} $4f^6 5d^1 \Rightarrow 4f^7 (^8S_{7/2})$ intra-ion emission. Both PL and PL excitation bands show a characteristic broad featureless structure, further broadened at increased temperatures due to strong electron-phonon coupling (Fig. 1). For Eu doped ZnS such an emission was not observed. This fact we explain as being due to the degeneracy of the first excited state, $4f^6 5d^1$, of the Eu^{2+} ion with the continuum of CB states and its consequent fast autoionization, as was demonstrated previously in a direct photo-ESR experiment for Eu^{2+} in the CdF_2 lattice [10]. Hence, the only stable excited state of Eu in ZnS is an exciton bound at the Eu^{2+} center (Fig. 2(a)). The appropriate emission band due to direct radiative recombination of the Eu bound exciton (BE) was observed [11].

In CaS the ground state of Eu^{2+} is "deeper" by ~ 0.5 eV and the first excited state is no longer a fully resonant state. In this system the ionization and recapture both proceed from and to the $4f^6 5d^1$ excited state. The BE state is either not formed or if it is formed it is unstable due to very rapid energy transfer to Eu^{2+} "core" states. The optical cross section for Eu^{2+} ionization is found to be relatively small and the excitation spectrum of Eu^{2+} emission is dominated by the direct $4f^7 \Rightarrow 4f^6 5d^1$ intra-ion transition (Fig. 2(b)).

Our data indicate that the position of Eu^{2+} ground state level, in respect to the band structure of host lattices, strongly influences the recombination and luminescence excitation mechanisms.

References

- [1] S. Tanaka, H. Deguchi, Y. Mikami, M. Shiiki, H. Kobayashi, *Proc. S. I. D.* **28**, 21 (1987).
- [2] H. Hartmann, *J. Cryst. Growth* **42**, 144 (1977).
- [3] M. Leskelä, M. Mäkelä, L. Niinistö, E. Nykänen, M. Tammenmaa, *Chemtronics* **3**, 113 (1988).
- [4] M. Godlewski, D. Hommel, *Phys. Status Solidi A* **95**, 261 (1986).
- [5] K. Świątek, M. Godlewski, D. Hommel, H. Hartmann, *Phys. Status Solidi A* **114**, 127 (1989).
- [6] P.B. Dorain, *Phys. Rev.* **120**, 1190 (1960).
- [7] K. Świątek, M. Godlewski, *Acta Phys. Pol.* **A77**, 95 (1990).
- [8] K. Świątek, A. Suchocki, M. Godlewski, *Appl. Phys. Lett.* **56**, 195 (1990).
- [9] L.L. Chase, *Phys. Rev. B* **2**, 2308 (1970).
- [10] M. Godlewski, D. Hommel, J.M. Langer, H. Przybylińska, *J. Lumin.* **24/25**, 217 (1981).
- [11] K. Świątek, M. Godlewski, D. Hommel, *Phys. Rev. B* **42**, 3628 (1990).