Inorganica Chimica Acta, *139* (1987) 261–263

Photoluminescence Study of Tb^{3+} Doped Alkaline Earth Sulfide Thin Films*

MILJA ASPLUND, JORMA HÖLSÄ,
MARKKU LESKELÄ**, LAURI NIINISTÖ†
and ERJA NYKÄNEN

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

Alkaline earth sulfides (MS = CaS, SrS and BaS) have been found to be suitable hosts for cathode tube phosphors but they have not replaced ZnS in large scale applications. Activated MS phosphors are also potential materials for powder type DC operated electroluminescent (EL) devices [1]. Recently, the alkaline earth sulfides doped with lanthanoids have been studied as EL materials in AC operated thin film devices [2–4]. The aim of the investigations was to find phosphors for a full color flat EL device.

The preparation of MS thin films by the traditional methods (e.g. sputtering or evaporation) is more difficult than that of ZnS which is the competing host material. The reason is the refractory nature of MS and their tendency to form non-stoichiometric compounds.

Lanthanoid ions, having allowed electronic transitions (Ce^{3+} and Eu^{2+}), can be successfully excited by an electric field in MS hosts, whereas for some reason the ZnS host favors ions with forbidden transitions (e.g. Sm^{3+} and Tb^{3+}) [5]. Promising results have been obtained with CaS:Ce^{3+} (green emission with maxima at 505 and 570 nm), SrS:Ce^{3+} (blue–green, 475 nm) and CaS:Eu^{2+} (red, 650 nm) [3, 6, 7]. Low EL brightness values have earlier been reported for CaS:Tb^{3+} but in a recent work much higher values have been obtained [8]. Recently, a review article on EL materials has appeared [9].

In the present work the Tb^{3+}-doped MS (M = Ca, Sr and Ba) thin films have been grown by the Atomic Layer Epitaxy (ALE) method. We have earlier grown lanthanoid-doped ZnS thin films by the same method [10, 11].

Experimental

Preparation of the MS:Tb^{3+} Thin Films

The thin films were grown on a glass substrate by the ALE method using the thd-chelates (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) of the alkaline earth metals and terbium as starting materials. The sulfur source used was H_2S. The substrate temperature was about 720 K. The activator content of the films was controlled by changing the interval of $Tb(thd)_3$ pulses between the $M(thd)_2$ and H_2S pulses. The terbium contents of the films used in this study were typically a few mole per cent. No co-activator was used to balance the difference in the oxidation states between Tb^{3+} and M^{2+}.

The quality of the thin films was studied by X-ray methods, as described earlier [10–12]. MS thin films of good crystallinity can be grown by the ALE method and the difficulties present in evaporation methods can be avoided. The results of X-ray diffraction studies have been presented elsewhere [13]. The film thicknesses and the activator contents were determined by X-ray fluorescence [12–14].

Optical Measurements

The luminescence of MS:Tb^{3+} (MS = Ca, Sr and Ba) thin films was excited by conventional UV radiation. A 200 W mercury lamp with wide-band filters provided a global excitation between 250 and 300 nm. This wavelength corresponds to the strong $4f^8 \rightarrow 4f^75d$ absorption band of the Tb^{3+} ion in MS.

The luminescence of the MS:Tb^{3+} thin films was recorded at two sample temperatures, both at the ambient and liquid nitrogen temperatures. The emission was dispersed by a 1-m Jarrell–Ash monochromator and detected by a Hamamatsu R374 photomultiplier. The visible wavelength range between 400 and 700 nm was scanned.

Results and Discussion

The Tb^{3+}-doped thin films of alkaline earth (Ca, Sr and Ba) sulfides show intense green luminescence under UV excitation (Fig. 1). The emission color is due to the strong $^5D_4 \rightarrow {}^7F_5$ transition between 544 and 551 nm. Supplementary lines corresponding to the transitions from the $^5D_4$ level to the $^7F_3$, $^7F_4$ and $^7F_6$ levels can be found near 623, 585 and 493 nm, respectively. The sample temperature has no significant effect on the color of the emission. The liquid nitrogen temperature usually enhances transitions from the higher excited $^5D_3$ level to the ^7F_J (J = 0–5) ground term, which correspond to the groups of lines in the blue region of the spectrum. The

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

**Present address: Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku, Finland.

†Author to whom correspondence should be addressed.

0020-1693/87/$3.50

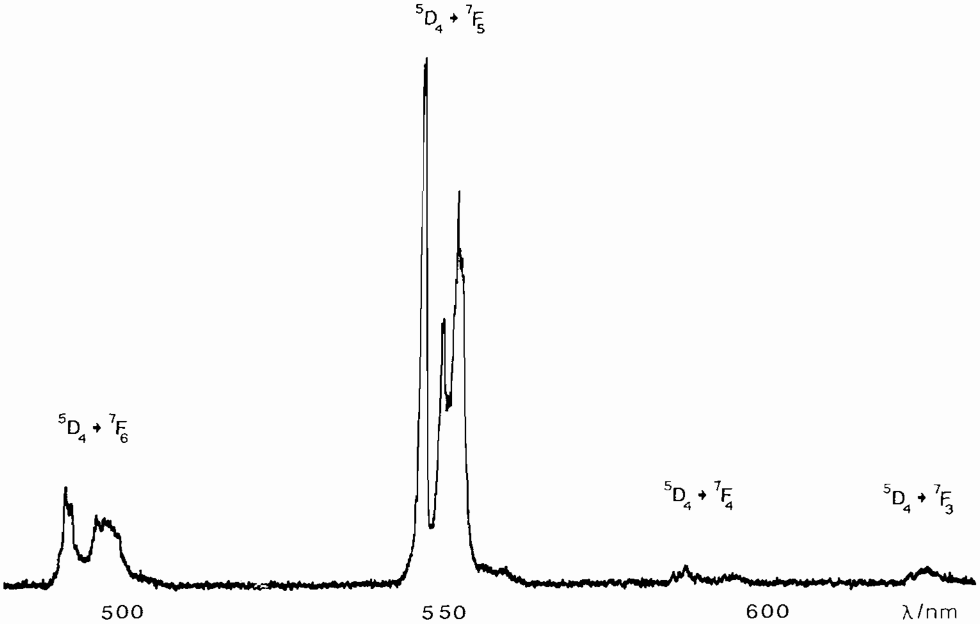

Fig. 1. Part of the photoluminescence spectrum of the CaS:Tb^{3+} thin film recorded at 77 K when excited with UV radiation between 250 and 300 nm.

absence of the $^5D_3 \rightarrow {^7F_J}$ transitions may be due to the relaxation of the excitation energy through multiphonon processes involving the lattice vibrations. Another means of de-excitation can occur through an interaction between the $4f^7 5d$ configuration which is at low energy in the Tb^{3+} ion.

The emission spectra of the Tb^{3+} ion in all alkaline earth sulfides studied are rather similar to one another. This indicates that the Tb^{3+} ions occupy sites of similar symmetry irrespective of the host matrix. The alkaline earth sulfides have a sodium chloride type structure with the host cation occupying a site of octahedral symmetry. As a consequence, the electric dipole transitions should in principle be forbidden for a Tb^{3+} ion in such a site due to the presence of the inversion symmetry. However, the introduction of a trivalent Tb^{3+} ion into an M^{2+} site creates distortions in the crystal structure due to the charge compensation effects. The distortions destroy the octahedral symmetry of the Tb^{3+} site, thus breaking the electric dipole transition rules and these transitions become weakly allowed.

There exist several ways to accomplish the charge compensation of the Tb^{3+} ion in an MS lattice, e.g. the creation of vacancies and/or interstitial ions, conserving, however, the overall stoichiometry of the bulk of the lattice. In any case, no preferred combination between the Tb^{3+} ion and the species of the charge compensation can be assumed. The great number of different Tb^{3+} sites leads to a complicated crystal field fine structure within the $^5D_4 \rightarrow {^7F_J}$ transitions, which is actually observed experimentally. The magnitude of the distortions due to the charge compensation seems to be rather limited since the sharp lines due to the transitions between the different Stark components form groups. The number of these groups of lines for the $^5D_4 \rightarrow {^7F_J}$ ($J = 3$–6) transitions corresponds to the splitting of the ^7F_J levels in an octahedral site symmetry, *i.e.* 3, 4, 4 and 6 for the J values equal to 3, 4, 5 and 6, respectively. The distortions and the weak splitting of the $^5D_4$ emitting level render the transition selection rules inefficient, which results in the presence of transitions between all Stark levels.

The conservation of the original octahedral site symmetry is supported also by the high intensity ratio between the $^5D_4 \rightarrow {^7F_5}$ and the pure electric dipole $^5D_4 \rightarrow {^7F_6}$ transitions. The $^5D_4 \rightarrow {^7F_5}$ transition has been shown to possess a considerable magnetic dipole origin being thus allowed in the presence of an octahedral symmetry.

The crystal field splittings of the ^7F_J levels amount to a few hundred cm^{-1} (160, 230, 240 and 320 cm^{-1} for the $^7F_3$, $^7F_4$, $^7F_5$ and $^7F_6$ levels, respectively) which indicates a relatively weak crystal field effect. The splitting of the emitting $^5D_4$ level is very weak since an increase in the sample temperature induced no supplementary lines on the high energy side of the $^5D_4 \rightarrow {^7F_J}$ transition measured at 77 K.

As a final remark it should be noted that the Tb^{3+} ion yields in alkaline earth sulfide matrices intense electroluminescence, too, and thus this activator/host combination appears to be a promising candidate for a green phosphor in EL devices.

Acknowledgements

The authors are indebted to Dr P. Caro and Dr P. Porcher (C.N.R.S., Meudon, France) for the use of the luminescence equipment. Financial aid from the Academy of Finland to one of the authors (J.H.) is gratefully acknowledged.

References

1 A. Vecht, *J. Cryst. Growth, 59,* 81 (1982).

2 W. A. Barrow, R. E. Coovert and C. N. King, *SID 84 Digest,* 249 (1984).

3 V. Shanker, S. Tanaka, M. Shiiki, H. Deguchi, H. Kobayashi and H. Sasakura, *Appl. Phys. Lett., 45,* 960 (1984).

4 H. Kobayashi, S. Tanaka, V. Shanker, M. Shiiki and H. Deguchi, *J. Cryst. Growth, 72,* 559 (1985).

5 S. Tanaka, H. Deguchi, A. Mikami, M. Shiiki and H. Kobayashi, *SID 86 Digest,* 29 (1986).

6 K. Tanaka, A. Mikami, T. Ogura, K. Taniguchi, M. Yoshida and S. Nakajima, *Appl. Phys. Lett., 48,* 1730 (1986).

7 Y. Tamura, J. Ohtaki, H. Kozawaguchi and B. Tsujiyama, *Jpn. J. Appl. Phys., 25,* L105 (1986).

8 M. Asplund, L. Hiltunen, M. Leskelä, L. Niinistö, E. Nykänen and M. Tammenmaa, to be published.

9 M. Leskelä and M. Tammenmaa, *Mater. Chem. Phys., 16,* 349 (1987).

10 M. Tammenmaa, T. Koskinen, L. Hiltunen, M. Leskelä and L. Niinistö, *Thin Solid Films, 124,* 125 (1985).

11 M. Tammenmaa, M. Leskelä, T. Koskinen and L. Niinistö, *J. Less-Common Met., 126,* 209 (1986).

12 H. Antson, M. Grasserbauer, M. Hamilo, L. Hiltunen, T. Koskinen, M. Leskelä, L. Niinistö, G. Stingeder and M. Tammenmaa, *Fresenius Z. Anal. Chem., 322,* 175 (1985).

13 M. Tammenmaa, H. Antson, M. Asplund, L. Hiltunen, M. Leskelä, L. Niinistö and E. Ristolainen, *J. Cryst. Growth,* in press.

14 M. Tammenmaa, Y. Ylirnokanen, M. Leskelä and L. Niinistö, *Anal. Chim. Acta,* in press.