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Electroluminescence in a Terbium Complex

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Electroluminescent devises consisted of two layers, a hole injecting diamine layer and an emitting Tb^{3+} complex of acetylacetonate layer, were fabricated by vacuum deposition. The EL cells exhibited characteristic bright Tb^{3+} luminescence with high efficiency at low drive voltage.

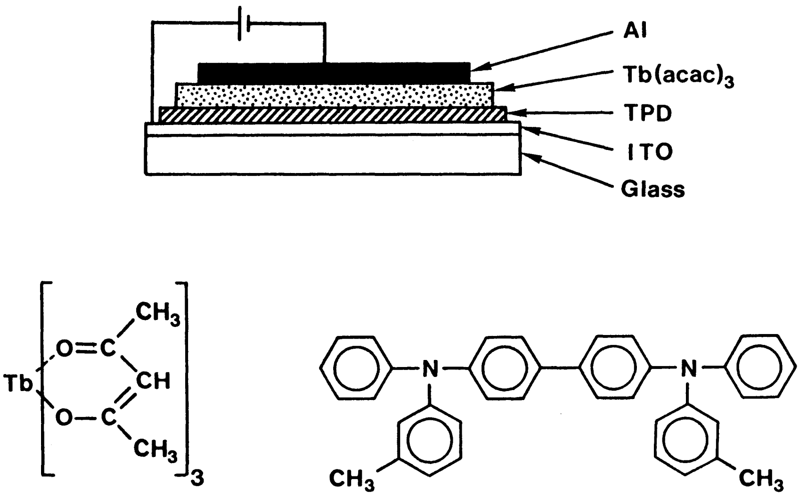
Electroluminescence (EL) in organic crystals has been investigated by a number of researchers for practical electroluminescent devices.1) One of the problems concerning these devices is their relatively high drive voltage (over 100 V); hence, this type of device is not practically useful yet.

Recently, Tang and VanSlyke2) demonstrated that the use of diamine layer for hole injection into the emitting layer significantly lowers the drive voltage to as low as few volt. Their device consisted of a double layer structure with a hole transporting diamine layer and a luminescent aluminum complex. Their recent study3) showed that doping the aluminum complex layer with organic luminescent dyes yields luminescence from the dopant materials with higher quantum efficiency.

Similar results were obtained by Adachi and his coworkers.4,5) Their devices consisted of three organic layers, a diamine layer for hole injection, a luminescent organic dye layer, and an electron injecting layer. By using appropriate luminescent dyes, they obtained desired luminescent colors such as blue, green and red. Their latest study6) showed that luminescent materials with hole transporting properties exhibit efficient EL without a hole transporting diamine layer. However, due to the broad nature of the luminescence spectra of organic dyes, the luminescent colors are somewhat dull and would not be the best suited for the actual display applications.

Our objective is to obtain bright and efficient EL devices with a narrow luminescent spectral band width. Thus we investigated the suitability of a terbium ion (Tb^{3+}) complex as a possible emitter. This metal ion is known to exhibit green photoluminescence with very sharp spectral bands and has been commonly used as a dopant in inorganic thin film EL devises.[7] Various Tb^{3+} complexes exhibit photoluminescence with high quantum efficiency and the properties of its complexes have been well studied in the solid state as well as in solutions.[8]

Our devise configuration and the molecular structures of the organic materials used in this study are shown in Fig. 1. The cell consisted of two layers, a diamine layer and an emitting layer, similar to the EL cell fabricated by Tang and VanSlyke.[2] The diamine was N,N'-diphenyl-N,N'-(3-methyl phenyl)-1,1'-biphenyl-4,4'-diamine (TPD) which was prepared according to the literature.[9] Tb(acetylacetonate)$_3$ (Tb(acac)$_3$) used as the emitter was synthesized by conventional method.



Tb(acac)$_3$ TPD

Fig. 1. Configuration of EL device and molecular structures of TPD and Tb(acac)$_3$.

The EL cells were fabricated by means of vacuum deposition. The organic layers including TPD and Tb(acac)$_3$ layers were successively deposited onto an ITO-coated glass plate (10-20 Ω/□, Hoya Co. Ltd.) kept at room temperature at 5.0×10^{-5} Torr. The thickness of the each layers were ca. 200 and 400 Å, respectively. The aluminum top electrode was finally deposited at 7.0×10^{-7} Torr. The emitting area was 1 cm^2. Luminance was measured with a Minolta luminance meter LS-110 at room temperature.

Bright green emission was observed from the EL cell when operated in a continuous dc mode (biased Al negative). As shown in Fig. 2, the spectrum had a line-like character which is characteristic luminescence of Tb^{3+} ion, and was found to be identical with the photoluminescence spectrum of the Tb(acac)$_3$. The strongest emission was peaking at 544 nm corresponding to the $^5D_4 \rightarrow ^7F_5$ transition of the Tb^{3+} ion. The spectral profile, the relative intensity of the each peak, was independent of the current density.

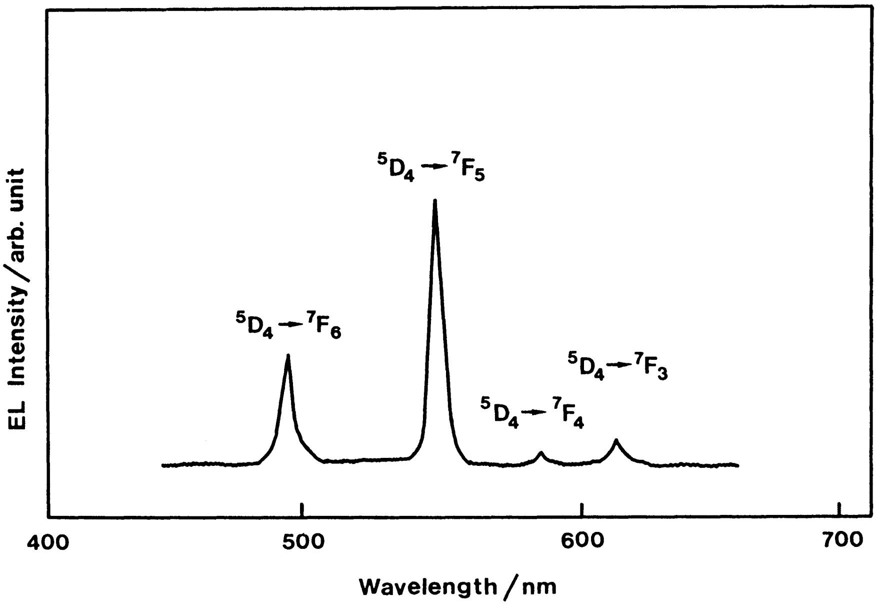


Fig. 2. Electroluminescence spectrum of ITO/TPD/Tb(acac)$_3$/Al.

The continuous dc current (I)-voltage (V) and brightness (B)-voltage (V) curves for the EL cell are shown in Fig. 3. The luminance was proportional to the injection current as well as the bias voltage. At 0.4 mA/cm^2, the luminance of 7 cd/m^2 was achieved, which is comparable to that of 10 cd/m^2 at 1 mA/cm^2 for the latest organic EL devises by Adachi et al.$^{6)}$ We used aluminum as an electorode because of its stability and easy handling. Replacing it with a lower work-function metal such as Mg or its alloies should reduce the drive voltage. Because we haven't optimized the configuration of the EL devise, the drive voltage, energy conversion efficiency, could be further improved.

It should be noted here that the stability of the EL cell was strongly dependent on the atmosphere. Under ambient atmosphere without any protection, the luminance decayed relatively fast (a few minutes) at a constant current. However the device in the argon atmosphere at liquid nitrogen temperature showed much longer lifetime (100 h or longer). Although the degradation mechanism is not fully understood at this moment, the degradation of both hole and electron injecting contacts has been suggested.$^{2)}$

In conclusion, we have made an EL device having sharp luminescent bands as well as high EL efficiency. We are currently working on other lanthanide metal ion complexes to obtain different luminescent colors such as red and blue.

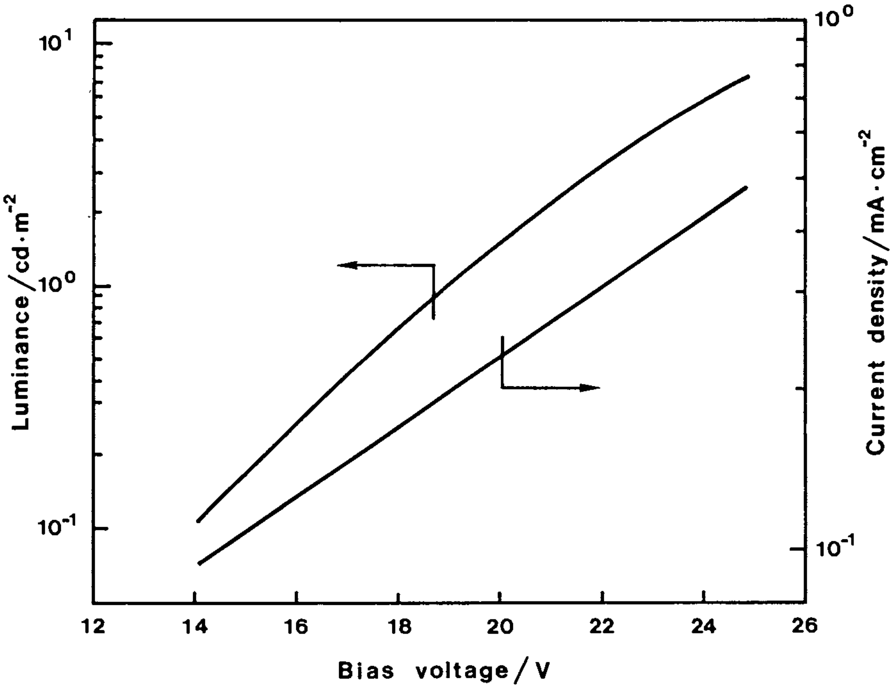


Fig. 3. Luminance-current-voltage characteristics for an ITO/TPD/Tb(acac)$_3$/Al cell.

References

1) J. Kalinowski, *Material Science*, 7, 43 (1981), and references therein.

2) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett*, 51, 913 (1987).

3) C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.*, 65, 3610 (1989).

4) C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys*, 27, L269 (1988).

5) C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys*, 27, L713 (1988).

6) C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, 55, 1489 (1989).

7) For example, T. Ogura, A. Mikami, K. Tanaka, K. Taniguchi, M. Yoshida, and S. Nakajima, *Appl. Phys. Lett.*, 48, 1570 (1986); T. Hirate, T. Ito, and M. Hikasa, *J. Appl. Phys.*, 57, 976 (1985); F. J. Bryant, and A. Krier, *Phys. Stat. Sol.*, 81, 681 (1984).

8) S. P. Sinha, "*Complexes of the Rare Earth*," Pergamon, London (1966).

9) M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.*, 88, 4707 (1984).

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