Sensors and Materials, Vol. 9, No. 1 (1997) 025–034
MYU Tokyo

S & M 0269

Filtered Full-Color Thin-Film Electroluminescent Device with ZnS:TbOF/ZnS:PrOF Phosphor Layers

Young-Jae Cho, Mikihiro Noma[1] and Yoshihiro Hamakawa[2]

Faculty of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Osaka 560, Japan
[1]Liquid Crystal Display Labs., Sharp Co., Ltd., 2613-1 Ichinomoto,Tenri, Nara 632, Japan
[2]Faculty of Science & Engineering, Ritsumeikan University, Kusatsu, Shiga 525, Japan

(Received May 26, 1995; accepted June 27, 1996)

Key words: filtered full-color thin-film EL device, ZnS:TbOF/ZnS:PrOF phosphor layer, RGB spectral components

A filtered full-color ZnS:TbOF/ZnS:PrOF thin-film electroluminescent (EL) device has been developed. Emission spectra of the device include the three primary-color spectral components, i.e., red, green and blue (RGB) lines. With the use of these spectral components, an attempt has been made to develop a full-color display by means of filtered color emission technology. Chromaticity coordinates of the green emission and the red emission from the filtered device are almost equal to those of a cathode ray tube (CRT), while chromaticity coordinates of the blue emission shift markedly toward those of green.

1. Introduction

Recently with the progress of electronic information processing, demand has rapidly grown for high-quality active flat-panel full-color display devices. The electroluminescent (EL) display device is one of the most promising candidates for responding to this demand. Oishi *et al.* have reported that with the tunable color ZnS:SmF_3/ZnS:TbF_3 EL device, the emission color can be gradually varied from green to red,[(1)] and Hamakawa *et al.* have reported a full-color ZnS:TmF_3/ZnS:SmF_3/ZnS:TbF_3 EL device showing 7 colors (red, green, blue, white, and 3 neutral tints).[(2)] The fabrication of the latter EL device has proven that a practical full-color EL device can be realized. There is, however, a problem in that the blue emission of the full-color EL device is not bright enough. The ZnS:TmF_3 phosphor layer of the full-color EL device emits very pure blue light, but its luminance is too low for practical purposes.[(3–4)] To solve this problem, some types of white-lightemitting EL displays used with color filters have been studied: for instance, SrS:Ce,Cl/ZnS:Mn,[5] SrS:Ce,K,Eu,[6] SrS:Pr,Ce,[7] and SrS:Ce/CaS:Eu.[8] These devices are able to produce the three primary colors, red, green, and blue (RGB), with color filters, but EL devices made from SrS or CaS phosphor do not have good stability against the humidity in air or a long lifetime. Therefore a full-color EL device with ZnS phosphor having good stability is desired.[9] In this work, a filtered full-color ZnS:TbOF/ZnS:PrOF EL device has been developed and its luminescence properties have been extensively investigated.

The ZnS:TbOF thin-film EL device emits bright green light and its spectrum consists of a green main line (542 nm), a blue line (488 nm), an orange line (584 nm), and a red line (619 nm).[10] Intensities of the blue line and the red line are much weaker than that of the green line. The ZnS:PrOF EL device emits white light which consists of a blue-green line (494 and 502 nm) and a red line (651 and 657 nm), but it does not have any green lines.[10]

Therefore the sum of those spectra will have three primary-color spectral components, a red, a green, and a blue line, due to the addition of the ZnS:PrOF emission to the ZnS:TbOF emission. This EL device filtered with RGB filters will thus show bright RGB emission.

2. Experimental

EL devices with the typical double insulating-layer structure were fabricated on glass substrates (NA40) coated with stripe-patterned indium-tin-oxide (ITO) transparent electrodes. Amorphous SiN_x:H insulating layers were prepared at 250°C by the plasma enhanced chemical vapor deposition (PECVD) method. Phosphor layers were deposited by the electron beam (EB) evaporation method, and two kinds of evaporation sources, 3 mol% ZnS:TbOF (ZnS powder doped with 1 mol% TbF_3 and 0.5 mol% Tb_4O_7) and 0.5 mol% ZnS:PrOF (ZnS powder doped with 0.166 mol% PrF_3 and 0.056 mol% Pr_6O_{11}), were prepared which were molded and sintered at 600°C in Ar atmosphere for 2 hours. Substrate temperature during evaporation was 350°C for the ZnS:TbOF phosphor and 200°C for the ZnS:PrOF phosphor. The phosphor layers were annealed at 500°C in vacuum for one hour after evaporation. Luminance of EL devices was measured using a luminance meter (Topcon BM-3) under 1 or 5 kHz sinusoidal excitation. EL spectra were measured by a spectrometer (Photal MCPD-1000) at 5 kHz.

3. Results

3.1 *Chromaticity coordinate simulation*

The authors have previously reported that the ZnS:TbOF EL device has more than three times higher luminance than a conventional ZnS:TbF_3 EL device.[11,12] Electroluminescence characteristics of a ZnS:PrOF EL device were also investigated and compared with those of a conventional ZnS:PrF_3 EL device. The results have clarified that the ZnS:PrOF EL device also has luminance twice as high as that of the ZnS:PrF_3 EL device. Figure 1 shows a comparison of luminance-voltage characteristics of the ZnS:TbOF EL device and

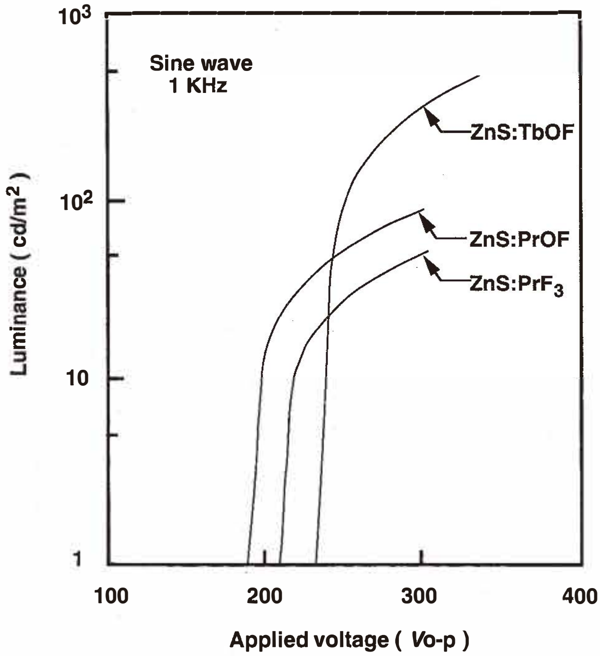

Fig. 1. Comparison of the luminance-voltage characteristics between the ZnS:TbOF EL device and the ZnS:PrOF EL device.

the ZnS:PrOF EL device. Both the ZnS:TbOF phosphor layer and the ZnS:PrOF phosphor layer were 6000 Å thick. Maximum luminance is approximately 500 cd/m^2 for the ZnS:TbOF EL device and 100 cd/m^2 for the ZnS:PrOF EL device at 1 kHz.

The emission spectrum of the ZnS:TbOF/ZnS:PrOF EL device was simulated on the assumption that the emission intensity of the ZnS:TbOF phosphor layer equals that of the ZnS:PrOF phosphor layer. Measured EL spectra of the ZnS:TbOF device and the ZnS:PrOF EL device are shown in Fig. 2. The ZnS:TbOF EL spectrum consists of four spectral components; a main green line, and a blue, an orange, and a red line. The ZnS:PrOF EL spectrum consists of two spectral components, a blue-green line and a red line. These measured spectra are normalized in equal-energy spectra, and then their sum is calculated and shown in Fig. 2. The calculated spectrum is observed to have three primary-color spectral components. Therefore it is possible to obtain bright pure RGB emission from the ZnS:TbOF/ZnS:PrOF EL device using a RGB filter.

Figure 3 shows the chromaticity coordinate simulation of the calculated spectrum using ideal filters on the Commission Internationale de l'Èclairage (CIE) 1931 chromaticity diagram. It was assumed that the ideal filters were able to transmit 100% of light in the transmittable wavelength region and 0 % outside that region.[7] Open circles in the figure

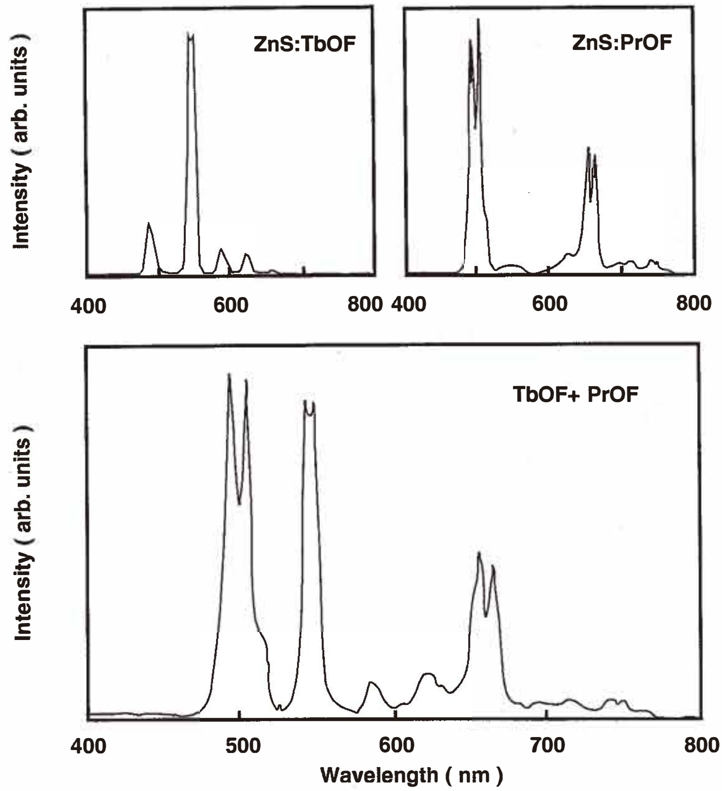

Fig. 2. Measured EL spectra of the ZnS:TbOF EL device and the ZnS:PrOF EL device (top) and calculated sum of those measured spectra (bottom).

indicate RGB of the CRT. Closed circles show the calculated RGB of the ZnS:TbOF/ ZnS:PrOF EL device with the ideal filter and without a filter. The original color of the device without a filter is not white but nearly green. The chromaticity coordinates of the green and the red emission of the device do not greatly depend on the kind of filter. This means that very pure green emission and pure red emission can be obtained using any kind of filter. On the other hand, the emission color of the device with the blue filter shifts from blue toward green as the wavelength increases in the transmittable region of the filter. Figure 3 shows that the longest wavelength required in the transmittable region of a blue filter to obtain blue emission with good color purity should be shorter than 500 nm.

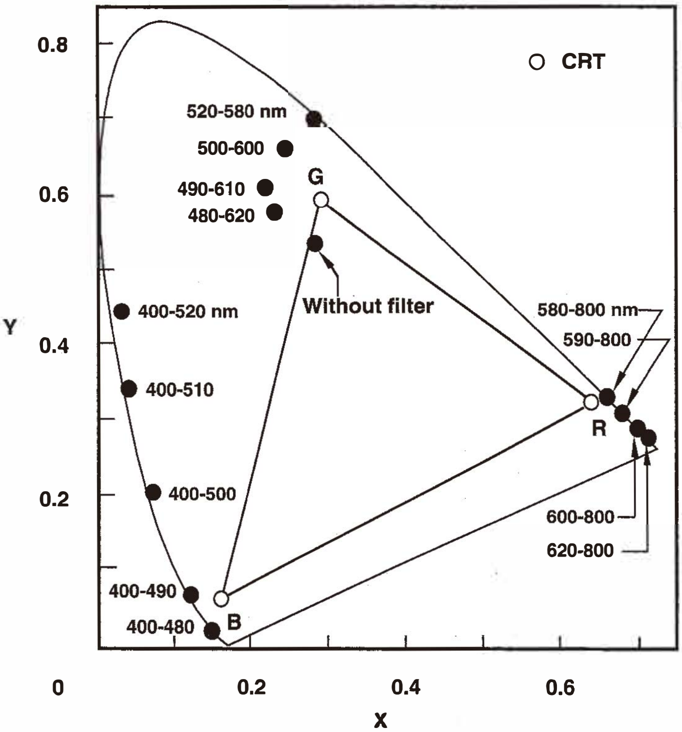

Fig. 3. Chromaticity coordinate simulation for the ZnS:TbOF/ZnS:PrOF EL device on the CIE chromaticity diagram.

3.2 *Electroluminescence property*

A cross-sectional view of the fabricated ZnS:TbOF/ZnS:PrOF EL device is shown in Fig. 4. The thickness of the ZnS:TbOF phosphor layer was reduced to half that of the ZnS:PrOF phosphor layer, since the luminance of the ZnS:TbOF EL device is about 5 times higher than that of the ZnS:PrOF EL device, as shown in Fig. 1.

An undoped ZnS buffer layer of 1000 Å was inserted between the phosphor layers to avoid any detrimental effects of nonradiative energy transfer among Tb luminescent centers and Pr luminescent centers. Filters covering this device were selected according to the simulation results in Fig. 3. A red filter and a green filter made of colored glass, and a blue multilayer thin-film filter cutting off light of wavelength longer than 500 nm were used. Transmittance properties of these filters are shown in Fig. 5.

Luminance-voltage characteristics of the ZnS:TbOF/ZnS:PrOF EL device driven at 5 kHz are shown in Fig. 6. The luminance at 30 volts more than threshold voltage (L_{30}) is 234 cd/m^2 and the maximum luminance is 336 cd/m^2. The values for L_{30} with the red filter, the green filter, and the blue filter (Lr_{30}, Lg_{30}, and Lb_{30}) are 37 cd/m^2, 138 cd/m^2, and 11 cd/m^2,

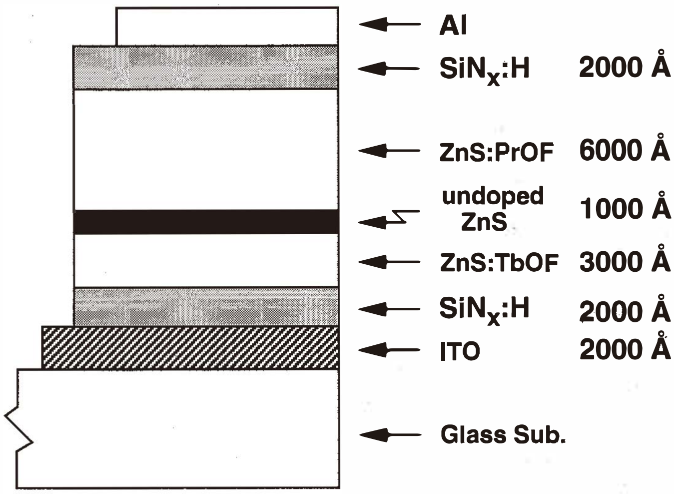

Fig. 4. Cross-sectional view of the fabricated ZnS:TbOF/ZnS:PrOF EL device.

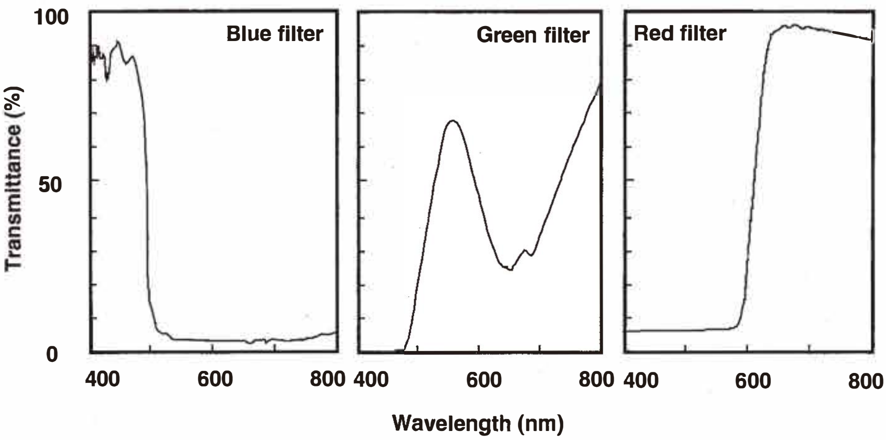

Fig. 5. Transmittance property of the filters covering the ZnS:TbOF/ZnS:PrOF EL device.

and maximum luminance values with the red filter, with green filter, and the blue filter are 52 cd/m^2, 150 cd/m^2, and 28 cd/m^2, respectively. The intensity ratio of the RGB emission (Lr_{30}, Lg_{30}, and Lb_{30}) was about R:G:B=3:13:1. The deviation from the intensity ratio of the CRT RGB emission, R:G:B=3:6:1, is due to the emission from the ZnS:PrOF layer being much weaker than that of the ZnS:TbOF layer in spite of the fact that the ZnS:PrOF layer is twice as thick as the other.

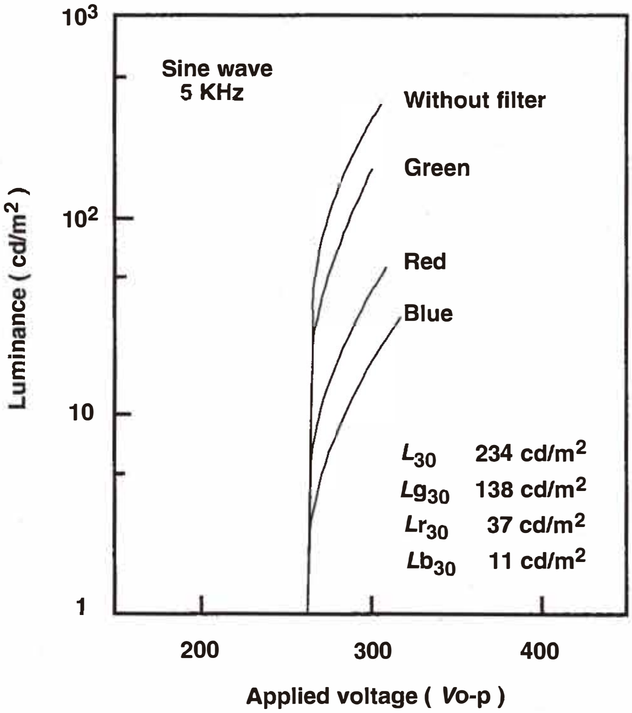

Fig. 6. Luminance-voltage characteristics of the ZnS:TbOF/ZnS:PrOF EL device.

Figure 7 shows the emission spectra of the ZnS:TbOF/ZnS:PrOF EL device without a filter and with a filter. The spectrum without a filter is similar to the simulation result shown in Fig. 2. The spectra with the red filter and the green filter are sufficiently transformed to show pure red emission and pure green emission. However the spectrum with the blue filter is not markedly changed; it has a small shoulder at 505 nm which decreases the color purity of the blue emission. Chromaticity coordinates of the spectra on the CIE chromaticity diagram are shown in Fig. 8. Pure red emission and pure green emission were obtained, and their chromaticity coordinates were almost the same as those of CRT red and green. Chromaticity coordinates of the original emission without a filter, the red emission, and the green emission agree well with those of the simulation shown in Fig. 3, but are a little whiter. Chromaticity coordinates of the blue emission shifted toward those of green emission more than did those in the simulation. The blue filter used in this experiment did not sufficiently cut off light of wavelengths longer than 500 nm, due to the longer peak of the split ZnS:PrOF blue-green line.

Greater improvement of emission efficiency of the ZnS:PrOF phosphor layer and further increase of the thickness ratio of the ZnS:PrOF phosphor layer to all the phosphor layers may yield the optimum emission intensity ratio, R:G:B=3:6:1. However it might be

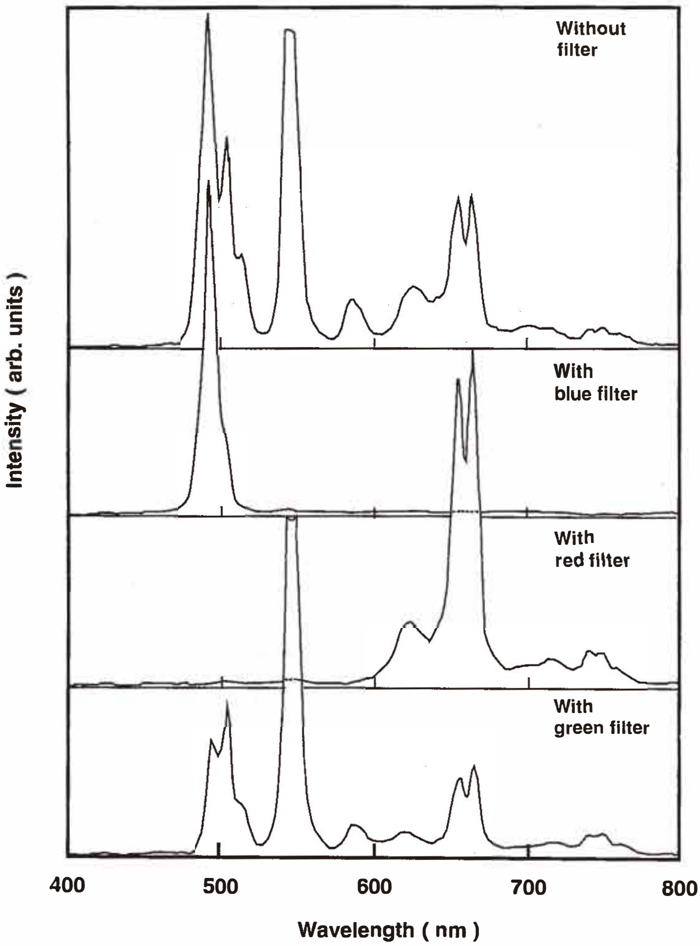

Fig. 7. Emission spectra of the ZnS:TbOF/ZnS:PrOF EL device without a filter and with a filter.

difficult to obtain blue emission of higher purity.

The emission colors of the filtered full-color ZnS:TbOF/ZnS:PrOF EL device, i.e., the original emission without a filter, the red emission, the green emission, and the blue emission, are shown in Fig. 9.

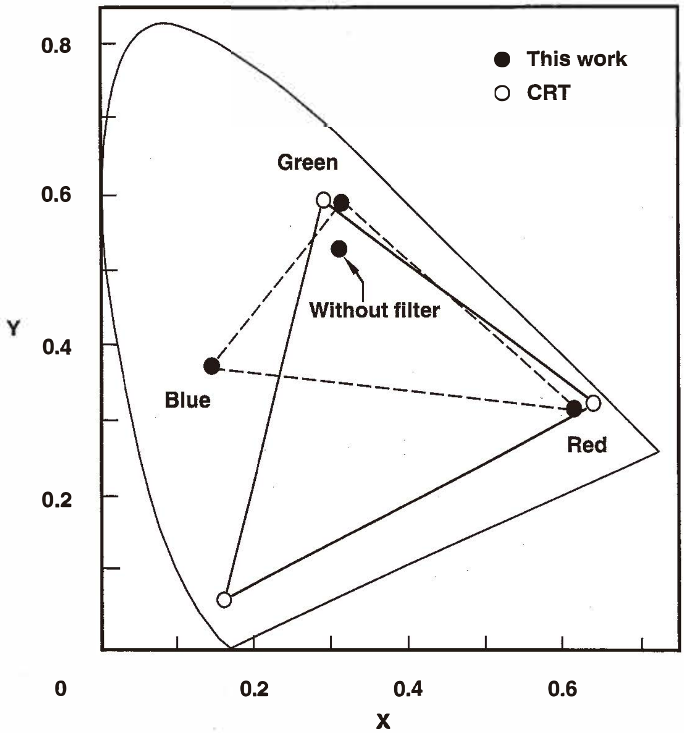

Fig. 8. Chromaticity coordinates of the emission spectra of the ZnS:TbOF/ZnS:PrOF EL device on the CIE chromaticity diagram.

4. Conclusions

A filtered full-color EL device combining ZnS:TbOF phosphor and ZnS:PrOF phosphor, whose spectra have RGB spectral components, has been proposed and fabricated. The luminance values of the ZnS:TbOF/ZnS:PrOF EL device, L_{30}, Lr_{30}, Lg_{30} and Lb_{30}, are 234 cd/m^2, 37 cd/m^2, 138 cd/m^2, and 11 cd/m^2, respectively. The intensity ratio of the RGB emission of ZnS:TbOF/ZnS:PrOF EL device was not the ideal ratio of R:G:B=3:6:1, but was R:G:B=3:13:1. The chromaticity coordinates of the red and green emissions from the filtered ZnS:TbOF/ZnS:PrOF EL device on the CIE chromaticity diagram are almost equal to those of the CRT, while the chromaticity coordinates of the blue emission shifted markedly toward those of green emission.

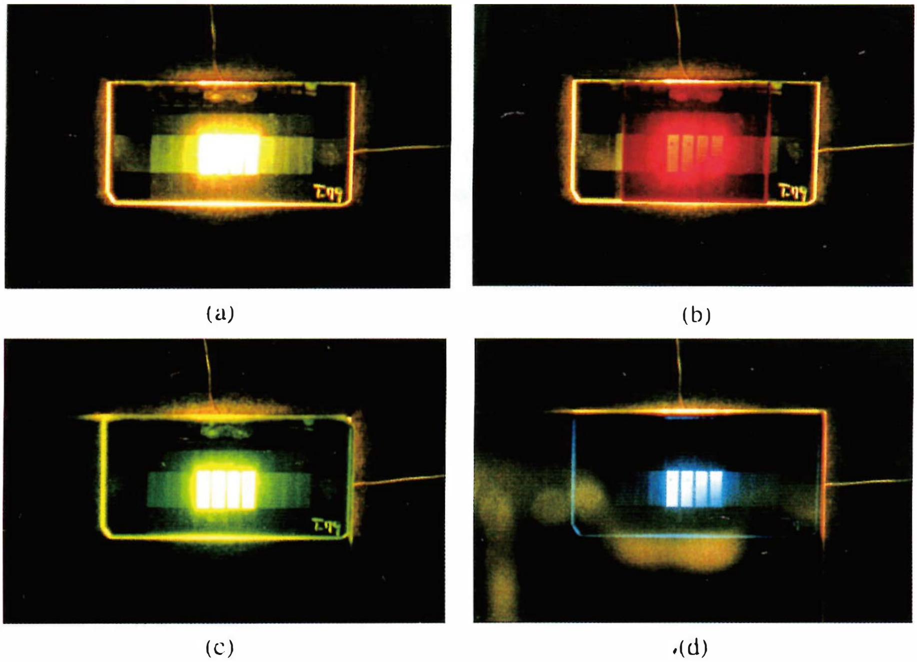

Fig. 9. Emission colors of the filtered full-color ZnS:TbOF/ZnS:PrOF EL device: (a) without filter, (b) red, (c) green, and (d) blue.

References

1 Y. Oishi, T. Kato and Y. Hamakawa: Extended Abstracts of the 15th Conf. on Solid State Devices and Materials, Tokyo (1983) p. 353.
2 Y. Hamakawa, R. Fukao and H. Fujikawa: Optoelectronics Devices and Technologies **3** (1988) 31.
3 T. Suyama, N. Sawara, K. Okamoto and Y. Hamakawa: Jpn. J. Appl. Phys. **21** (1982) Suppl. 21-1, 383.
4 K. Hirabayashi, H. Kozawaguchi and B. Tsujiyama: Jpn. J. Appl. Phys. **26** (1987) 1472.
5 S. Tanaka, Y. Mikami, H. Deguchi and H. Kobayashi: Jpn. J. Appl. Phys. **25** (1986) 225.
6 S. Tanaka, H. Yoshiyama, J. Nishiura, S. Ohshio, H. Kawakami and H. Kobayashi: Appl. Phys. Lett. **51** (1987) 1661.
7 Y. Abe, K. Onisawa, K. Tamura, T. Nakayama, M. Hanazono and Y. A. Ono: Jpn. J. Appl. Phys. **28** (1989) 1373.
8 Y. A. Ono, M. Fuyama, K. Onisawa, K. Tamura and M. Ando: J. Appl. Phys. **66** (1989) 5564.
9 K. Takahashi, K. Shibuya and A. Kondo: J. Crystal Growth **117** (1992) 979.
10 E. W. Chase, R. T. Hepplewhite, D. C. Krupka and D. Kahng: J. Appl. Phys. **40** (1969) 2512.
11 M. Noma, S. Hosomi, S. H. Sohn and Y. Hamakawa: 5th International Conf. on II – VI Compounds, Welb-29, Okayama (1991).
12 M. Noma, S. Hosomi, S. H. Sohn and Y. Hamakawa: J. Crystal Growth **117** (1992) 1030.