(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 249 942 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **87108638.5**

(51) Int. Cl.[4]: **H05B 33/14**

(22) Date of filing: **16.06.87**

(30) Priority: **19.06.86 JP 141473/86**

(43) Date of publication of application: **23.12.87 Bulletin 87/52**

(84) Designated Contracting States: **DE FR GB**

(71) Applicant: **TOYO SODA MANUFACTURING CO., LTD.**
No. 4560, Ooaza Tonda Shinnanyo-shi
Yamaguchi-ken(JP)

(72) Inventor: **Takahashi, Koyata**
7-37-17, Sagamiono
Sagamihara-shi Kanagawa(JP)
Inventor: **Ohnuki, Yukio**
3-18-6, Nakamachi
Machida-shi Tokyo(JP)
Inventor: **Kondoh, Akio**
1775, Okada
Atsugi-shi Kanagawa(JP)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4 P.O. Box 86 07 67
D-8000 München 86(DE)

(54) Thin film electroluminescent layer material.

(57) Disclosed is a thin film electroluminescent layer of a thin film electroluminescent device comprising, as a light-emitting medium, a body of a mixture of ZnS and at least one sulfide selected from MgS, CaS, SrS and BaS. The ZnS and the selected sulfide are doped with a transition metal or rare earth element which is optically active in the matrix. This EL device has good moisture resistance and weatherability and is capable of emitting a color with a high brightness.

EP 0 249 942 A2

THIN FILM ELECTROLUMINESCENT LAYER MATERIAL

The present invention relates to a thin film electroluminescent layer of a thin film electroluminescent (EL) display device which shows electroluminescence (EL) under the application of an AC voltage. More particularly, it relates to an improved thin film electroluminescent layer of a thin film EL device which comprises a transparent electrode, a dielectric layer or layers, an electroluminescent layer or layers and a back face electrode. The improved thin film electroluminescent layer comprises as a light-emitting medium a body of a mixture of ZnS and at least one sulfide selected from MgS, CaS, SrS and BaS, doped with a transition metal or rare earth element which is optically active in the light-emitting medium. Moreover, the present invention relates to a process for the preparation of a thin film electroluminescent layer of a thin film EL device, which comprises forming a thin film electroluminescent layer from a compound of a transition metal or rare earth element which is optically active in a light-emitting medium, ZnS and at least one sulfide selected from MgS, CaS, SrS and BaS by the vacuum deposition or sputtering method.

In the field of thin film EL devices driven by an AC voltage, to improve the insulation voltage resistance, luminescence efficiency, and operation stability, an EL device having a double dielectric layer structure has been developed in which an electroluminescent layer of ZnS or ZnSe doped with Mn is inserted between films of a dielectric material such as Al_2O_3 , Y_2O_3 or TiO_3 , and the luminescent characteristics of this EL device have been investigated. Research has been carried out into, especially, an electroluminescent layer of ZnS doped with Mn. Recently, an electroluminescent layer comprising CaS or SrS instead of ZnS as the light-emitting medium has attracted attention as a means of realizing a multi-color EL panel. For example, an electroluminescent layer comprising CaS doped with Eu emits a red luminescence, and an electroluminescent layer comprising SrS doped with Ce emits a greenish blue luminescence. However, these devices have problems in that the hygroscopicity of the light-emitting medium is higher than that of ZnS and the light-emitting medium is readily hydrolyzed. These properties increase the defect density of the elctroluminescent layer composed of this light-emitting medium, with the result that the luminance or durability of the device is degraded. Furthermore, Ce, which is a dopant for a green or blue luminescence, is more easily doped in CaS or SrS than in ZnS, and in the case of CaS or SrS, an electroluminescent layer emitting a luminescence at a high brightness is provided. In contrast, ZnS is stable as the light-emitting medium but has a problem in that certain dopants such as Ce are little doped in this light-emitting medium. Accordingly, it is desired to develop a light-emitting medium capable of overcoming the problems of these known light-emitting mediums, namely a light-emitting medium easily doped with a dopant and having an excellent moisture resistance and excellent weatherability.

The crystal form of a IIa-VIb group compound such as CaS or SrS is of the sodium chloride type and the crystal form of a IIb-VIb group compound is of the wurtzite or zinc blend type. It is known that different compounds of the same crystal form relatively easily form a solid solution. However, there have been few reports on the crystallinity or crystal structure of a film formed on a substrate by using a sintered mixture of compounds differing in crystal form, for example, by the vacuum deposition or sputtering method.

The IIa-VIb group compounds and IIb-VIb group compounds have quite different crystal forms, but when a mixture of ZnS and SrS containing a dopant is used as the film-forming material and a thin film electroluminescent layer is prepared by the vacuum deposition or sputtering method, the light-emitting medium of the resulting thin film electroluminescent layer can exhibit the light-emitting medium characteristics of both SrS and ZnS. Accordingly, we prepared a thin film EL device having a double dielectric layer structure by using a compound of a transition metal or rare earth element which is optically active in a light-emitting medium, ZnS and at least one sulfide selected from MgS, CaS, SrS and BaS as the vacuum deposition or sputtering material, and examined the electroluminescence characteristics of the thin film EL device. As the result, it has been found that the device has good EL characteristics.

It is a primary object of the present invention to provide a thin film electroluminescent layer of a thin film EL device which has good moisture resistance and weatherability and is capable of emitting a color with a high brightness.

In accordance with the present invention, there is provided a thin film electroluminescent layer of a thin film EL device comprising, as light-emitting medium, a body of a mixture of ZnS and at least one sulfide selected from MgS, CaS, SrS and BaS. The ZnS and the selected sulfide are doped with a transition metal or rare earth element which is optically active in the matrix.

This thin film electroluminescent layer of a thin film EL device is prepared by a process which comprises the step of forming a thin film electroluminescent layer from a compound of a transition metal or rare earth element which is optically active in a light-emitting medium, ZnS and at least one member selected from MgS, CaS SrS and BaS by the vacuum deposition or sputtering method.

Figure 1 is a structural diagram illustrating the basic structures of a thin film EL device;

Fig. 2 illustrates the electroluminescence characteristics of a thin film EL device wherein the electroluminescent layer is the film of a mixture of ZnS and SrS doped with CeF_3 according to the present invention;

Fig. 3 illustrates the electroluminescence spectrum of the above-mentioned thin film EL device;

Fig. 4 is a chromaticity diagram based on the electroluminescence spectrum shown in Fig. 3; and,

Fig. 5 shows an X-ray diffraction pattern of a thin film electroluminescent layer, in which (A) shows an X-ray diffraction pattern of a thin film electroluminescent layer composed of a film of a mixture of ZnS and SrS doped with CeF_3 according to the present invention and (B) shows an X-ray diffraction pattern of a thin film electroluminescent layer composed of SrS doped with CeF_3.

A thin film electroluminescent layer of a thin film EL device comprising ZnS, which is a II-VI group compound, doped with a compound of a transition metal or rare earth element such as Mn, Tb, Sm or Ce, have been studied. Compared with other II-VI group compounds, such as CaS, ZnS has a low hygroscopicity, is difficult to decompose, and is chemically stable, and ZnS has a sufficiently large band gap. Accordingly, ZnS is suitable as the light-emitting medium of the electroluminescent layer. Namely, if electroluminescent layers are composed of ZnS doped with various dopants, thin film EL devices emitting various colors can be prepared. For example, thin film electroluminescent layers formed by doping with HoF_3 , ErF_3 , SmF_3 , TbF_3 , NdF_3 , TmF_3 or the like emit colors such as red, blue, or green, but the blue color does not have sufficient luminance, and thus improvement is desired. Especially, in thin film EL devices emitting the three primary colors, that is, red, blue, and green, an increase of brightness and a prologation of life are desired. In order to attain this object, it is necessary to not only modify the dopant but also improve the light-emitting medium. SrS has an inferior chemical stability to ZnS, but a thin film EL device prepared by doping SrS with CeF_3 emits a blue color and a brightness of this blue color is higher than the brightness of the blue luminescence of the thin film EL device having an electroluminescent layer of ZnS doped with TmF_3. However, in order to prolong the life of the thin film EL device, preferably the light-emitting medium per se is chemically stable. Accordingly, with a view to improving the light-emitting medium used for the filmy electroluminescent layer for preparing a thin film EL device having a high luminance and an excellent moisture resistance and weatherability, we tried to combine ZnS with at least one sulfide selected from MgS, CaS, SrS and BaS, to provide a matrix having both the properties of SrS or the like suitable for the blue luminescence and the good chemical stability of ZnS.

In the electroluminescent body, the ratio of ZnS to the sulfide selected from MgS, CaS, SrS and BaS is preferably 0.5/99.5 to 99.5/0.5 by mole, and more preferably 90/10 to 95/5 by mole.

As the transition metal or rare earth element which is optically active in the light-emitting medium and contained as a dopant in the composite body of the electroluminescent layer of the present invention, there can be mentioned, for example, cerium, holmium, erbium, samarium, terbium, neodymium, thulium and manganese. The amount of the transition metal or rare earth element is CeF_3 , HoF_3 , ErF_3 , SmF_3 , TbF_3 , NdF_3 , TmF_3 , and MnF_3.

The electroluminescent layer of the thin film EL device the present invention can be prepared by subjecting a mixture of a dopant, ZnS and at least one sulfide selected from MgS, CaS, SrS, and BaS directly to vacuum deposition or other appropriate operation. Alternatively, the electroluminescent layer can be prepared by subjecting a dopant, ZnS, and at least one sulfide selected from MgS, CaS, SrS, and BaS, independently without mixing, to the multiple vacuum deposition or a similar operation. In view of the adaptability to the operation of forming the thin film EL device, preferably a sputtering or vacuum deposition method using as the target a sintered mixture of ZnS and at least one sulfide selected from MgS, CaS, SrS and BaS, which contains a dopant, is adopted. A suitable compound of a transition metal or rare earth element can be used as the dopant.

The so-formed body is ordinarily a solid solution consisting of one phase, but sometimes the thin film luminescent layer is composed of two or more phases differing in crystal form.

According to the present invention, there can be provided a thin film EL device having a thin film electroluminescent layer having good durability characteristics such as moisture resistance and weatherability. Moreover, thin film EL devices emitting various colors with a high brightness can be prepared by using various dopants. For example, if a thin film electroluminescent layer composed of a body of a mixture of ZnS and SrS, doped with CeF_3, is used, a thin film EL element emitting color close to blue, with a high brightness, can be prepared.

The present invention will now be described in detail with reference to the following examples, that by no means limit the scope of the invention.

Example 1

At first, a sputtering target for preparing an electroluminescent layer was prepared. SrS powder having a purity of 99.9%, ZnS having a purity of 99.9%, and CeF_3 having a purity of 99.99% were mixed for 30 minutes to obtain a powdery mixture. The powdery mixture was formed into a sputtering target by the hot press method. By using this target for an electroluminescent layer and a target of Al_2O_3 for a dielectric layer, a film layer having a double insulation structure was formed on a transparent electrode in an Ar atmosphere by the sputtering method to prepare a thin film EL device.

The EL device prepared in this example is shown in Fig. 1. Namely, this EL device was constructed by forming many band-like transparent electrodes 2 in parallel on a glass substrate 1, forming a first dielectric layer 3 of Al_2O_3 to a thickness of 2000 to 3000 Å on the transparent electrode 2, laminating an electroluminescent layer 4, composed of a CeF_3-incorporated film of a mixture of SrS and ZnS, to a thickness of 8000 to 10000 Å on the layer 3, forming a second dielectric layer 5 of Al_2O_3 to a thickness of 2000 to 3000 Å, and vacuum-depositing a back face electrode 6 of Al in the form of bands extending orthogonal to the transparent electrodes 2.

The so-constructed thin film EL device was heat-treated at 500°C in an Ar atmosphere for 1 hour, and the electroluminescence characteristics of the EL device were examined by applying sinusoidal voltage at 5 kHz. The dependence of the luminance on the applied voltage (V_{rsm}) is shown in Fig. 2. Curve (A) in Fig. 2 is a luminance-voltage curve just after application of the sinusoidal voltage to the EL device. The threshold voltage was 152 V and the luminance at V_{rms} = 182 V was 160 cd/m^2. Curve (B) is a brightness-voltage characteristic curve obtained after application of sinusoidal voltage at V_{rms} = 182 V to the EL device for 10 hours. Although the threshold voltage and the luminence are changed by aging, as is apparent from Fig. 2, the characteristic curve shown a similar feature compared with that before aging.

The luminescence spectrum of the luminescent color of this EL device is shown in Fig. 3, and the chromaticity diagram based on this luminescence spectrum is shown in Fig. 4. As is apparent from these Figs., the luminescence color of this EL device was a bluish green color and was in agreement with the luminescence colour of an SrS thin film electroluminescent layer having CeF_3 as the luminescence center.

The crystal structure of the electroluminescent layer of this thin film EL device was examined by X-ray diffractometry. The X-ray diffraction pattern is shown in Fig. 5-(A). For comparison, the X-ray diffraction pattern of the SrS electroluminescent layer doped with CeF_3, which emits a bluish green luminescence, is shown in Fig. 5-(B). The latter EL device was prepared in the same manner as described above with respect to the former EL device. It is well-known that the SrS film prepared on a substrate by the vacuum deposition method is the sodium chrolide type crystal. The X-ray diffraction pattern of the SrS film prepared for comparison with that of the ZnS film by the sputtering method in the present example Fig. 5(B) was substantially in agreement with the X-ray diffraction pattern of the SrS film prepared by the vacuum deposition, and it was confirmed that the crystal form of SrS film prepared by the sputtering was the same as SrS film prepared by the deposition. In the X-ray diffraction pattern of the electroluminescent layer of a mixture of ZnS and SrS doped with CeF_3, a peak assigned to the wurtzite structure or zinc blend structure inherent to the ZnS film was not observed, and this X-ray diffraction pattern was substantially in agreement with the X-ray diffraction pattern of the SrS film shown in Fig. 5(B). The composition of this film layer of the present invention has the sodium chloride type crystal structure as the SrS film, and Sr element in the SrS crystal lattice is partially substituted by Zn.

Example 2

A thin film EL device comprising as the electroluminescent film a film of a mixture of ZnS and CaS, doped with CeF_3, was prepared according to the process disclosed in Example 1. This EL device emitted a green luminescence with high brightness as the EL device comprising as the electroluminescent layer the film of a mixture of ZnS and SrS, doped with CeF_3, shown in Example 1.

Claims

1. A thin film electroluminescent layer of a thin film electroluminescent device comprising, as a light-emitting medium, a body of a mixture of ZnS and at least one sulfide selected from the group consisting of MgS, CaS, SrS and BaS; said ZnS

and said selected sulfide being doped with a transition metal or rare earth element which is optically active in the light-emitting medium.

2. A thin film electroluminescent layer according to claim 1, wherein the ratio of the ZnS to the selected sulfide in the body is in the range of 0.5/99.5 to 99.5/0.5 by mole.

3. A thin film electroluminescent layer according to claim 1, wherein the amount of the transition metal or rare earth element doped in the body is in the range of 0.01% to 5.0% based on the weight of the body.

4. A process for the preparation of a thin film electroluminescent layer of a thin film electroluminescent device, which comprises forming a thin film electroluminescent layer from a compound of a transition metal or rare earth element which is optically active in a light-emitting medium, ZnS and at least one sulfide selected from the group consisting of MgS, CaS, SrS and BaS by the vacuum deposition or sputtering method.

Fig. 1

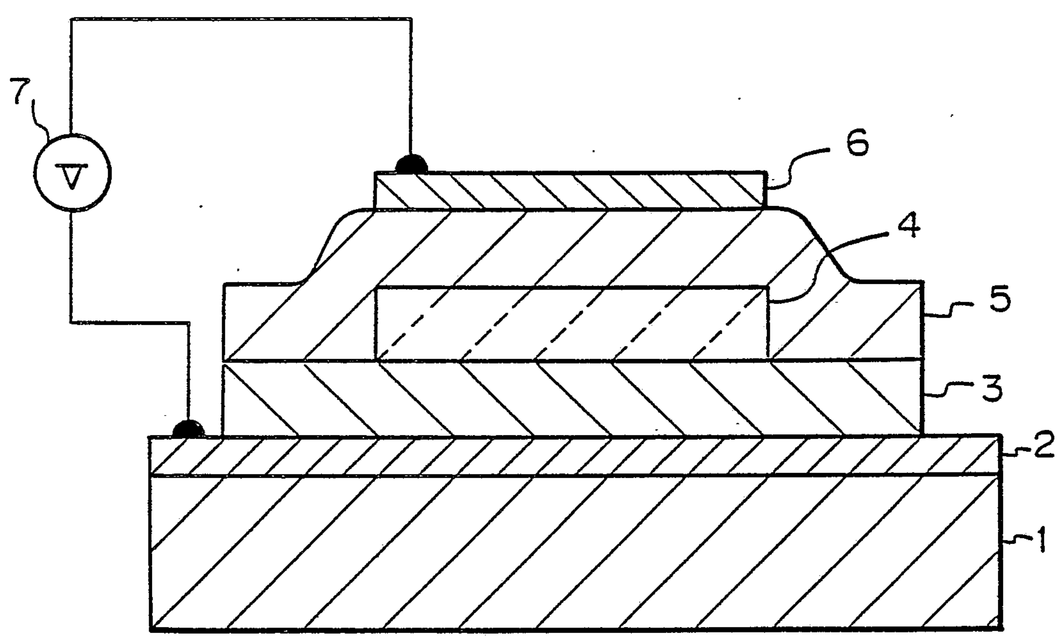
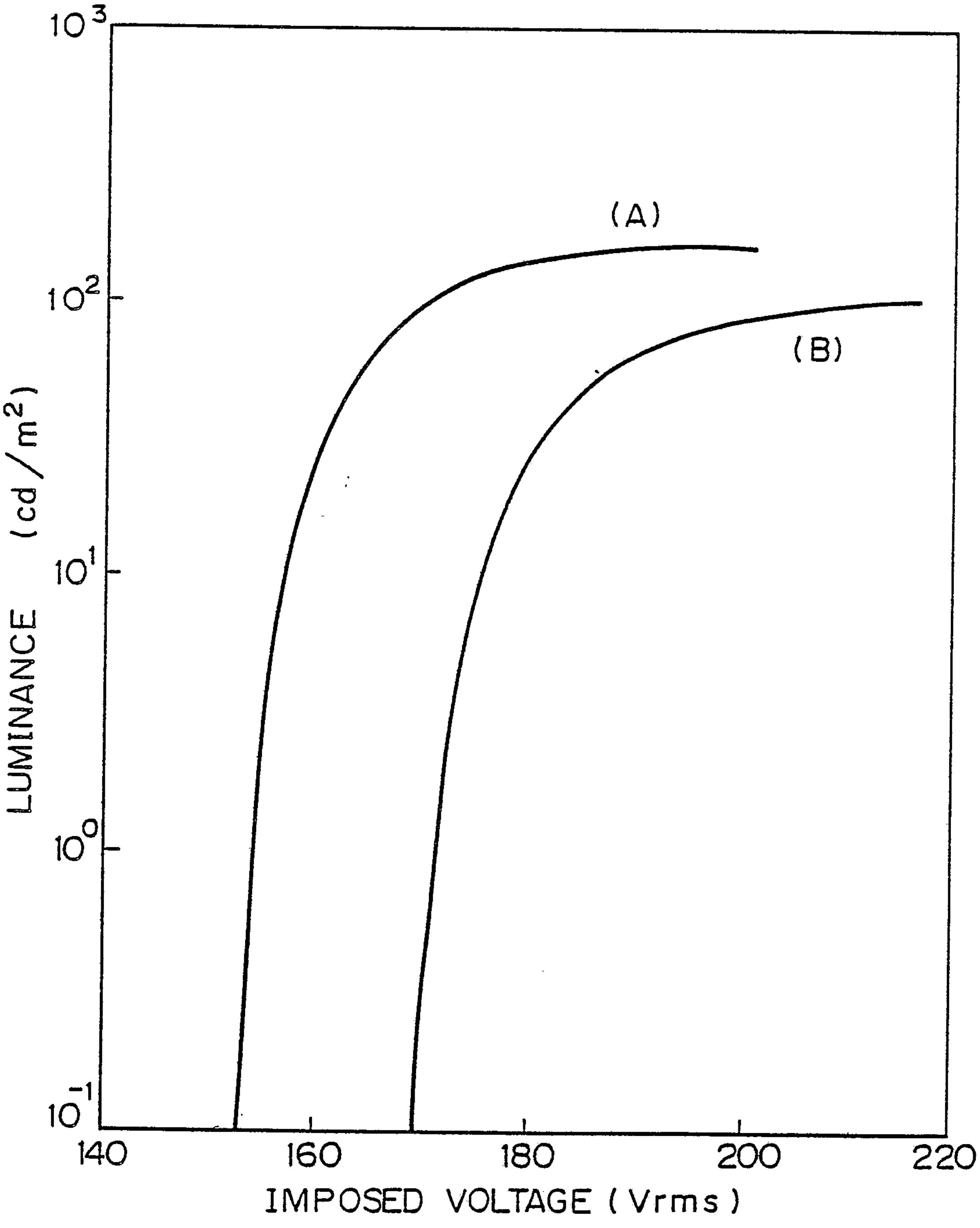


Fig. 2



10^3
10^2
10^1
10^0
10^{-1}
LUMINANCE (cd/m²)
(A)
(B)
140
160
180
200
220
IMPOSED VOLTAGE (Vrms)

Fig. 3

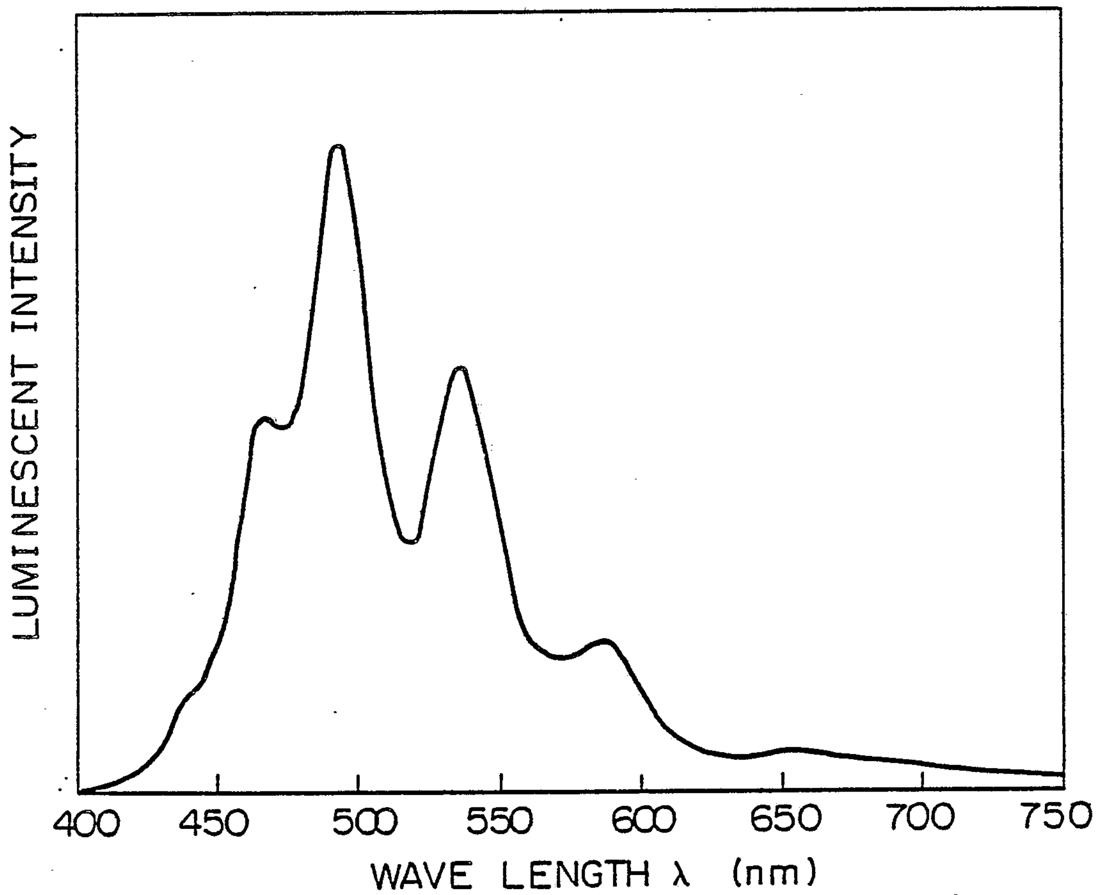
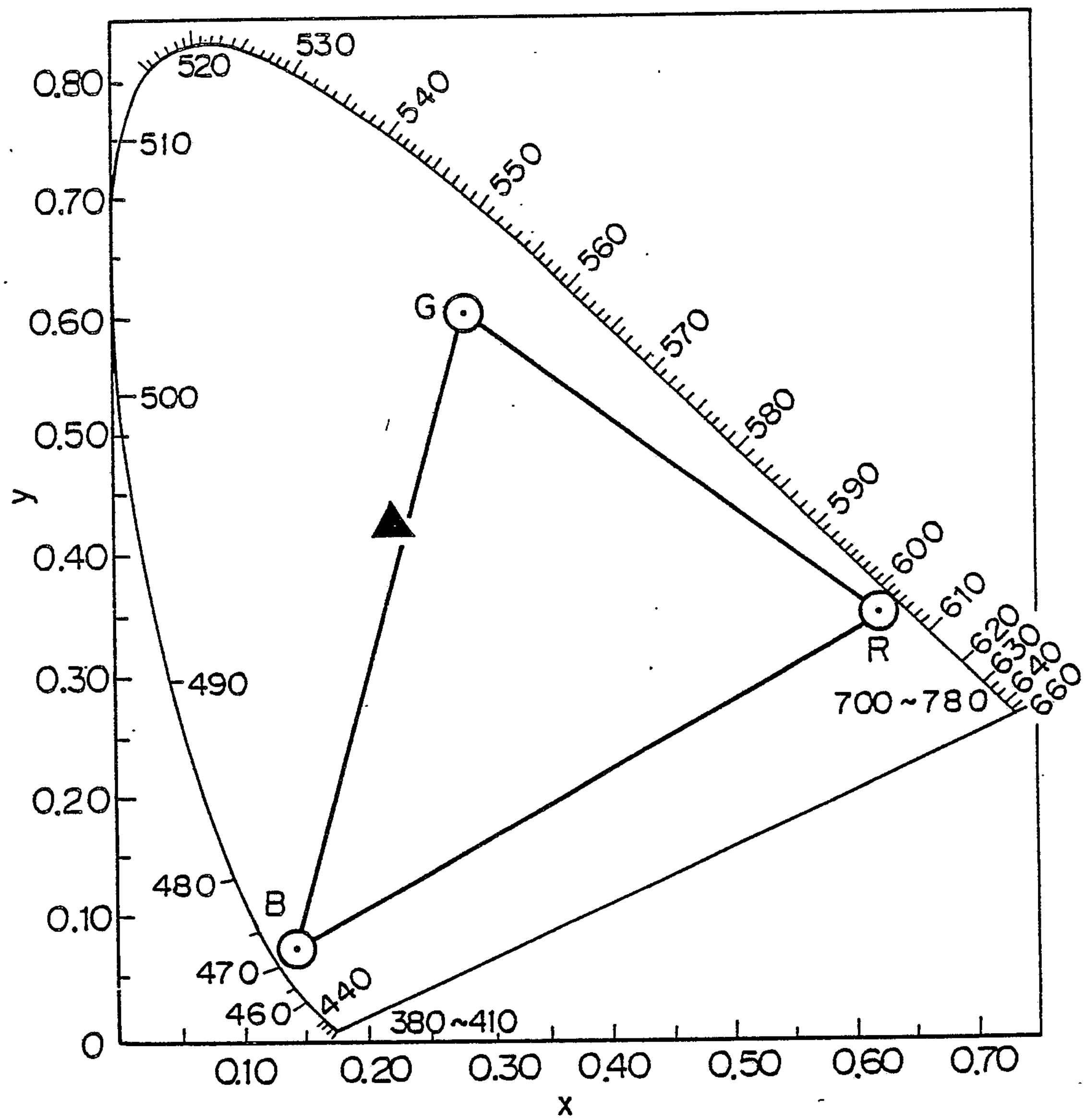

LUMINESCENT INTENSITY
400
450
500
550
600
650
700
750
WAVE LENGTH λ (nm)

Fig. 4



520
530
540
550
560
570
580
590
600
610
620
630
640
660
700~780
510
500
490
480
470
460
440
380~410
G
B
R
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
y
0.10
0.20
0.30
0.40
0.50
0.60
0.70
x

Fig. 5