P-143: High-Luminous Efficiency Full-Color Emitting $GdVO_4$:Eu, Er, Tm Phosphor Thin FIlms

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Abstract

High-luminous efficiency full-color emissions in photoluminescence (PL) were obtained in $GdVO_4$ phosphor thin films co-doped with various amounts of Eu, Er and/or Tm and postannealed at approximately 1000°C. The $GdVO_4$:Eu,Er,Tm phosphor thin films were deposited on thick $BaTiO_3$ ceramic sheets by r.f. magnetron sputtering using powder targets and postannealed in an air atmosphere. The rare earth (RE) content (RE/(Gd+V+RE) atomic ratio) in the oxide phosphor thin films was varied in the range from 0.1 to 2 at.%. It was found that the excitation of $GdVO_4$:Eu,Er,Tm thin films is attributed to band-to-band transition. A white PL emission was obtained in a $GdVO_4$:Eu,Er,Tm thin film with Eu, Er and Tm contents of 0.2, 0.7 and 1 at.%, respectively: CIE chromaticity color coordinates, (X=0.352 and Y=0.351). In addition, a white emission was obtained in a thin-film electroluminescent (TFEL) device made with this thin film.

1. Introduction

Recently, we reported gadolinium vanadate ($GdVO_4$) to be a promising host material for oxide phosphors [1,2]. A high-efficiency blue emission in photoluminescence (PL) and cathodoluminescence (CL) was newly developed using thulium-activated $GdVO_4$ ($GdVO_4$:Tm), in particular, as a thin-film. It should be noted that YVO_4 is well known as an excellent host material for rare earth-activated oxide phosphors in a powder form such as YVO_4:Eu [3]. We have also reported that multicomponent oxides composed of $GdVO_4$ and YVO_4 are promising host materials for rare earth-activated oxide phosphors because they have the same tetragonal system crystalline structure [4,5]. A high-luminous efficiency for red, green or blue emissions in PL and CL was obtained in $Y_{1-X}Gd_XVO_4$ phosphor thin films doped with Eu, Er or Tm, respectively. In addition, full-color emissions in PL were obtained in $Y_{1-X}Gd_XVO_4$:Eu,Er,Tm phosphor thin films prepared by controlling the contents of Eu, Er and Tm and the composition (X) [6].

In this paper, we describe the preparation of full-color emitting $GdVO_4$ phosphor thin films deposited by magnetron sputtering with co-doping of Eu, Er and/or Tm and postannealed. In addition, $GdVO_4$:Eu, Er, Tm thin films that exhibited white electroluminescence (EL) and PL were demonstrated.

2. Experimental

$GdVO_4$ thin films co-doped with rare earth elements such as Eu, Er and/or Tm were deposited on thick $BaTiO_3$ ceramic sheets by r.f. magnetron sputtering using powder targets. Mixtures of V_2O_5 and Gd_2O_3 and dopant (rare earth oxides such as Eu_2O_3, Tm_2O_3 and Er_2O_3) powders calcined at 1000°C in an Ar atmosphere were used as the target. The sputter deposition was carried out under the following conditions: atmosphere, pure Ar; pressure, 6 Pa; r.f. power, 140 W; and substrate temperature, 350°C. The thickness of all deposited $GdVO_4$ phosphor thin films was approximately 1 μ m. The rare earth (RE) content (RE/(Gd+V+RE) atomic ratio) in the phosphor thin films was varied in the range from 0.1 to 2 at.%. The deposited films were postannealed at 1000°C in an air atmosphere for 1 h in order to improve the luminescent characteristics.

The crystalline structure and the crystallinity of the phosphor thin films were investigated by X-ray diffraction (XRD) using a conventional X-ray unit with a copper anode. The PL emission and the excitation spectra of the thin films were measured using a spectrofluophotometer (Shimadzu RF-5300 PC). In addition, the chromaticity color coordinates for PL emission were measured under uv excitation (337 nm) from a N_2 laser using a chromaticity meter (TOPCON BM-7). The EL characteristics were investigated using a single-insulating-layer TFEL device structure consisting of an oxide phosphor thin-film emitting layer and a thick $BaTiO_3$ ceramic sheet insulating layer that also functioned as the substrate [7]. The EL characteristics of the TFEL devices were measured using a Sawyer-Tower circuit, a power meter, and a conventional luminance meter.

3. Multicolor emissions from co-doped $GdVO_4$ thin films

Figure 1 shows PL emission and excitation spectra of an Er-activated $GdVO_4$ ($GdVO_4$:Er) thin film postannealed at 1000°C. The spectral shape of the PL emission was independent of the excitation wavelength when it was within the excitation spectrum. It was found that the excitation spectra of $GdVO_4$:Tm and $GdVO_4$:Eu phosphor thin films, exhibiting a blue and a red PL emission, respectively, were approximately the same, as shown in Fig. 1. The observed excitation spectrum consisting of two peaks may be attributed to the band-to-band transition in $GdVO_4$ [2]. Figure 2 shows the CIE chromaticity color coordinates for the red, green and blue emissions observed from $GdVO_4$:Eu, $GdVO_4$:Er and $GdVO_4$:Tm phosphor thin films, respectively. This suggests that $GdVO_4$ phosphors co-doped with these rare earth elements could exhibit multicolor emissions in PL; the emission color can

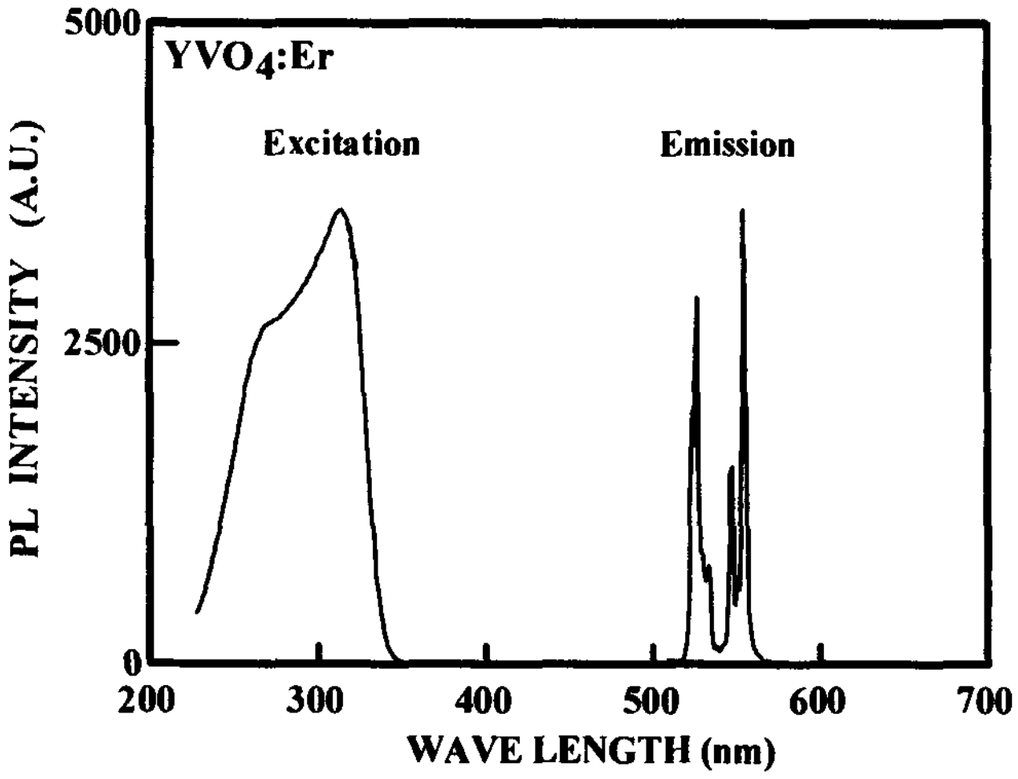

Fig. 1 PL emission and excitation spectra of a $GdVO_4$:Er thin film.

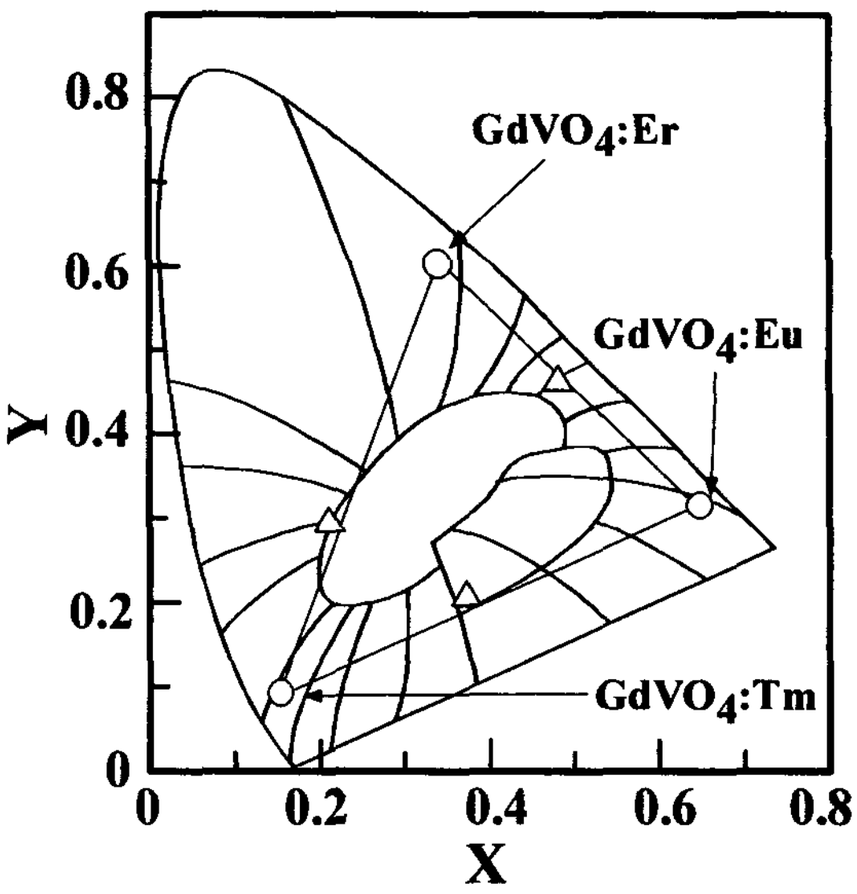

Fig. 2 CIE chromaticity color coordinates of PL emission from $GdVO_4$ phosphor thin films co-doped with Eu, Er and/or Tm.

be controlled by the kind as well as the amount, *i.e.*, the atomic ratio, of doped rare earth elements. For example, the emission color observed from Eu and Er co-doped $GdVO_4$ ($GdVO_4$:Eu,Er) phosphor thin films changed from red to green as the Eu/Er atomic ratio in the films was increased. In addition, multicolor emissions from green to blue and blue to red were obtained in $GdVO_4$:Er,Tm and $GdVO_4$:Tm,Eu phosphor thin films by increasing the Tm/Er and Eu/Tm atomic ratios, respectively.

As an example, Figs. 3 (a), (b) and (c) show PL excitation and emission spectra in a $GdVO_4$:Eu,Er, a $GdVO_4$:Er,Tm and a $GdVO_4$:Tm,Eu phosphor thin film, respectively, all postannealed at 1000℃. All of these thin films had the following contents: Eu, 0.2 at.%; Er, 0.7 at.%; and Tm, 1 at.%. It should be noted that the

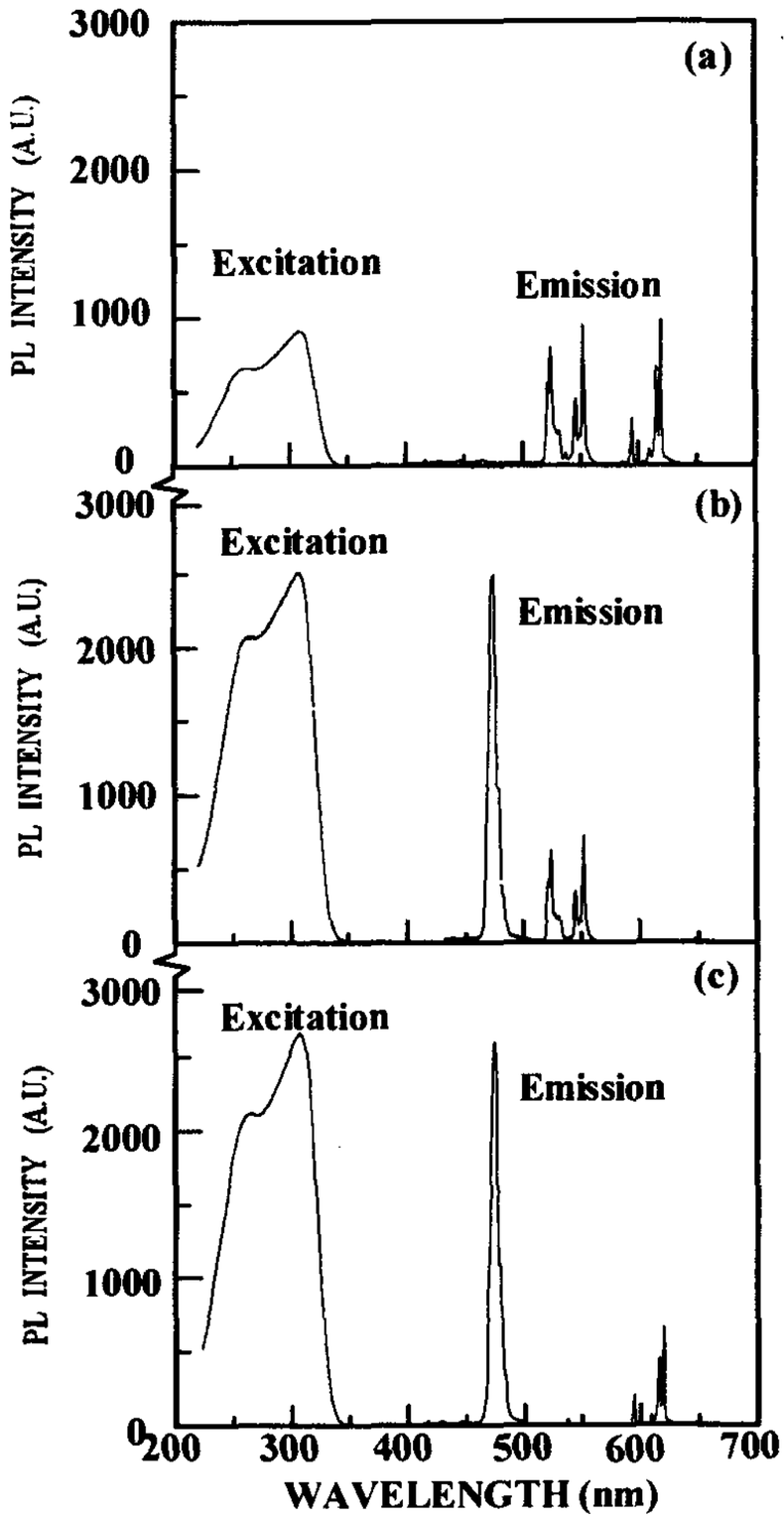

Fig. 3 PL emission and excitation spectra from (a) $GdVO_4$:Eu,Er, (b) $GdVO_4$:Er,Tm and (c) $GdVO_4$:Tm,Eu thin films.

spectral shapes of the PL emissions remained relatively unchanged when the excitation was applied with any wavelength within the excitation spectra. The CIE chromaticity color coordinates for PL emissions from these thin films are indicated in Fig. 2. In addition, it was found that high-efficiency multicolor emissions in PL could be obtained by varying the amount of Eu, Er or Tm co-doped into $GdVO_4$ phosphor thin films. The resulting CIE chromaticity color coordinates of the obtained multicolor emissions correspond to locations on the triangle indicated in the CIE chromaticity diagram shown in Fig. 2.

Although the obtained PL intensities of the co-doped $GdVO_4$ phosphors were found to be strongly dependent on the postannealing temperature, the spectral shapes of PL emissions were relatively independent of the temperature. PL emissions were observed when the co-doped phosphor thin films were postannealed above approximately 800℃; the intensities of PL emissions increased as the postannealing temperature was increased, reached a peak at approximately 1000℃, and then decreased with further increases of the temperature. As an

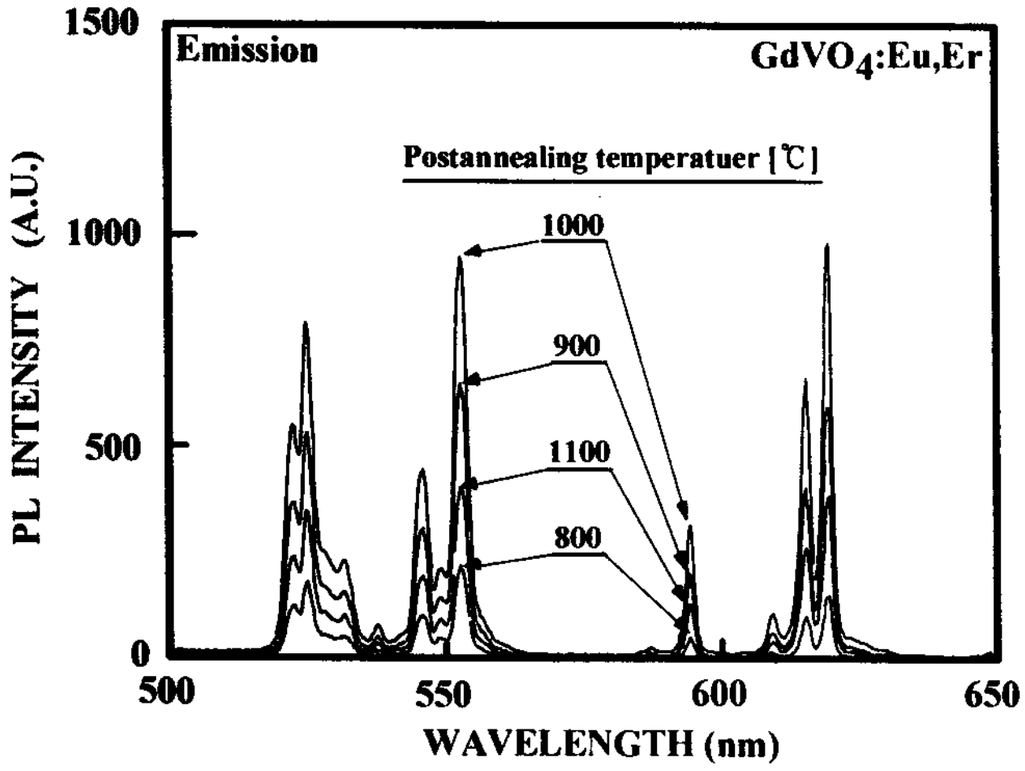

Fig. 4 Postannealing temperature dependence of PL emission spectra for $GdVO_4$:Eu,Er thin films.

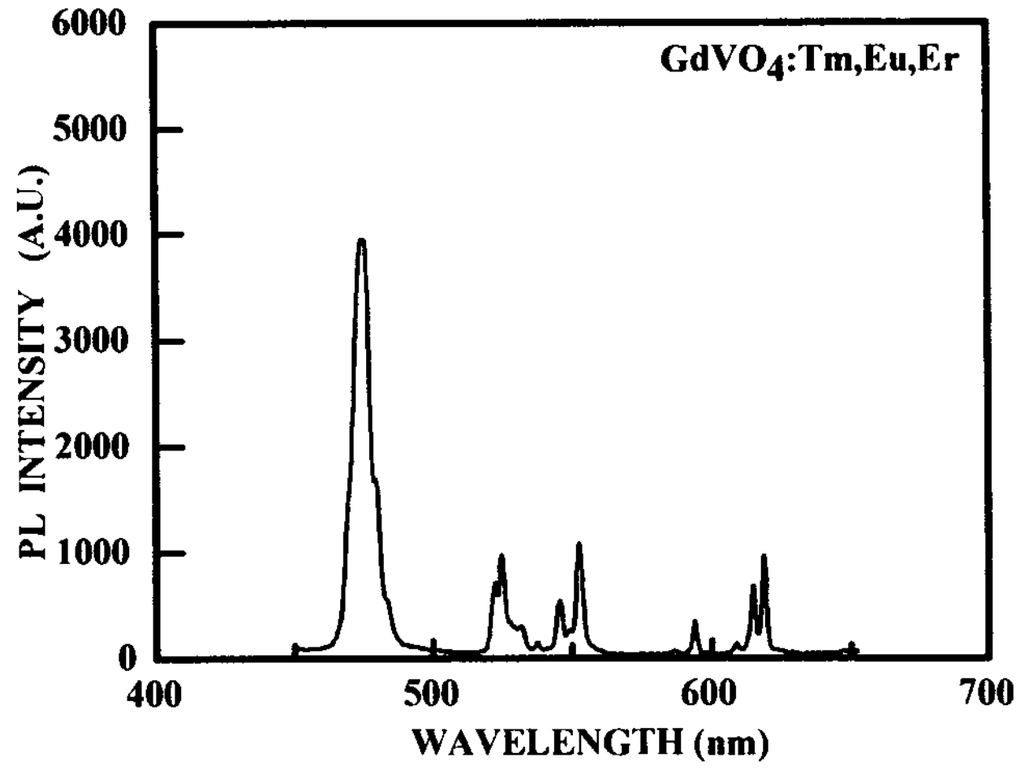

Fig. 6 PL emission spectrum of a $GdVO_4$:Eu,Er,Tm thin film.

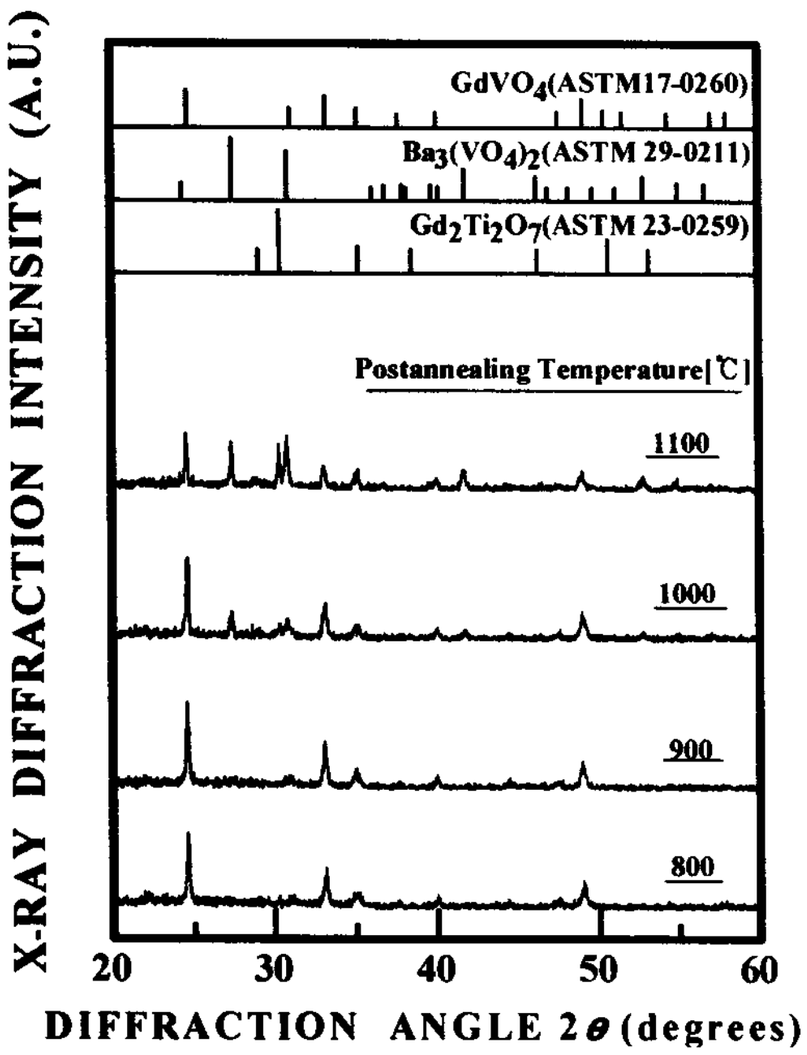

Fig. 5 Postannealing temperature dependence of XRD patterns for $GdVO_4$:Eu,Er thin films.

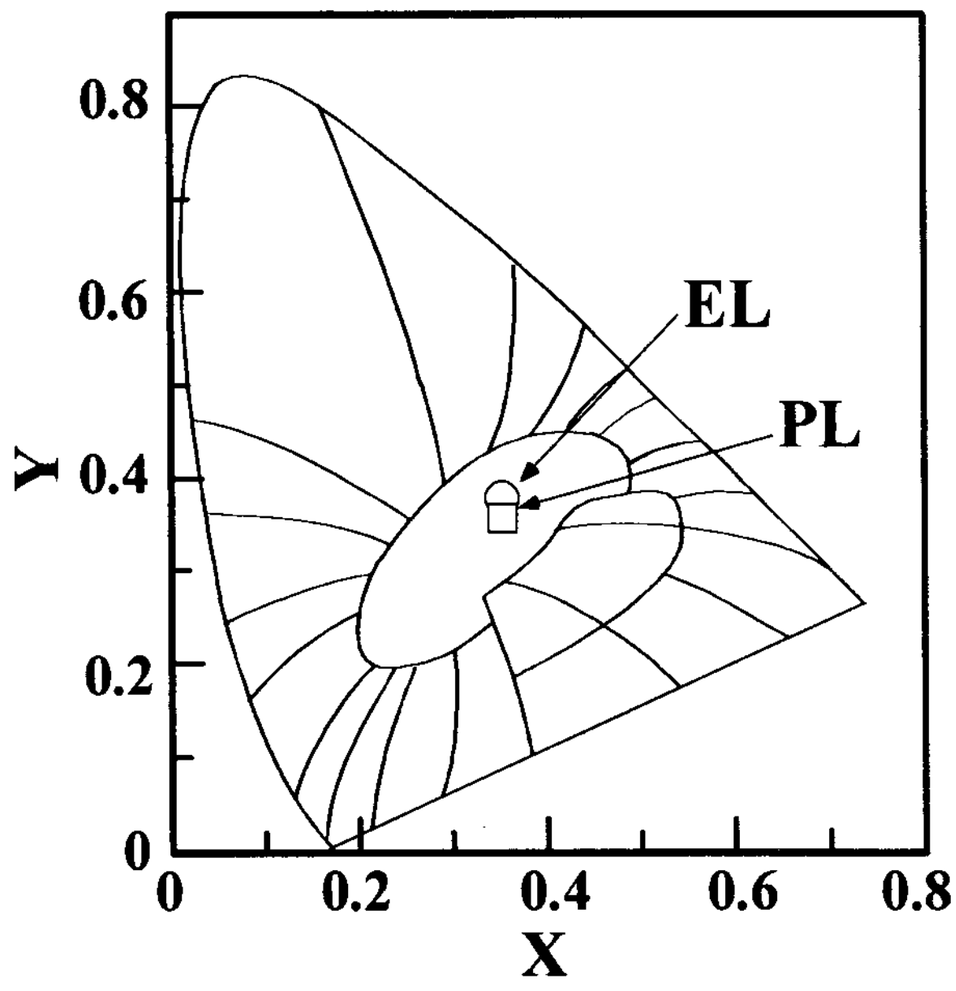

Fig. 7 CIE chromaticity color coordinates of PL and EL emissions from a $GdVO_4$:Eu,Er,Tm phosphor thin film.

example, Fig. 4 shows PL emission spectra as a function of the postannealing temperature for $GdVO_4$:Eu,Er thin films prepared with Eu and Er contents of 0.2 and 0.7 at.%, respectively. The obtained intensities of PL emissions from the phosphor thin films were mainly related to the crystallinity of $GdVO_4$, as evidenced by x-ray diffraction (XRD) analyses. As an example, XRD patterns as a function of the postannealing temperature are shown in Fig. 5 for the $GdVO_4$:Eu,Er thin films shown in Fig. 4. All XRD peaks observed from the phosphor thin films postannealed at a temperature up to approximately 1000°C were identified as coming from the $GdVO_4$ lattice, whereas new peaks observed from the films postannealed above approximately 1050°C were related to a new compound resulting from a chemical reaction with the $BaTiO_3$ substrate.

4. White emission from $GdVO_4$:Eu,Er,Tm thin films

The development of phosphors capable of emitting three colors (red, green and blue; RGB) is essential in order to realize full color emissions without color filters. In order to obtain color emissions that correspond to the entire area inside the triangle indicated in Fig. 2, it is necessary to prepare $GdVO_4$ phosphor

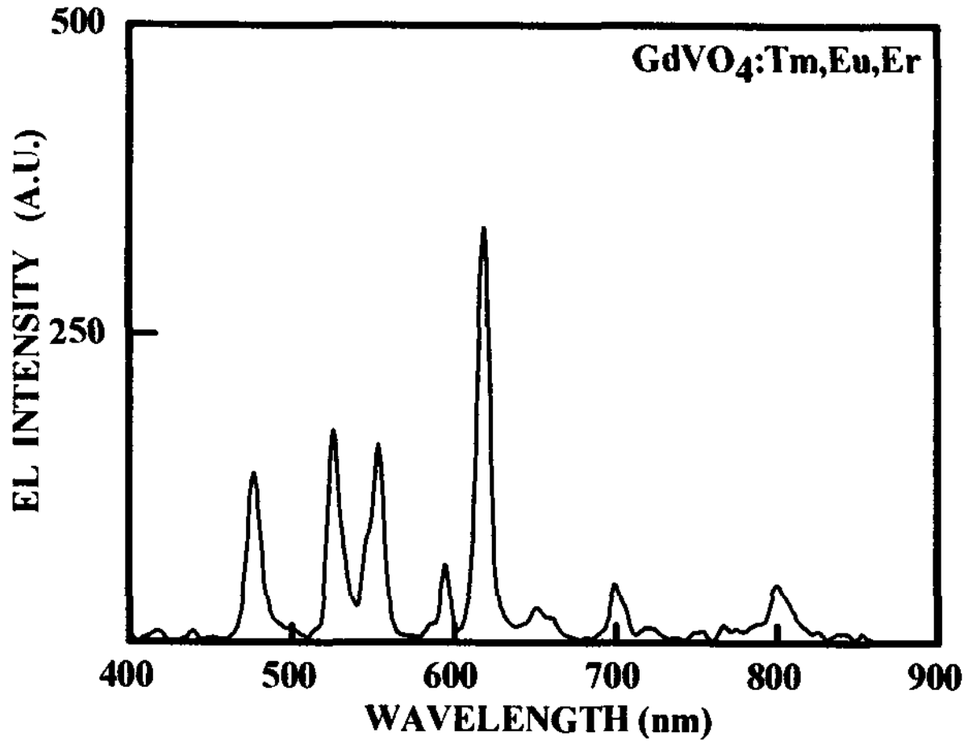

Fig. 8 Typical EL emission spectrum of a $GdVO_4$:Eu,Er,Tm TFEL device.

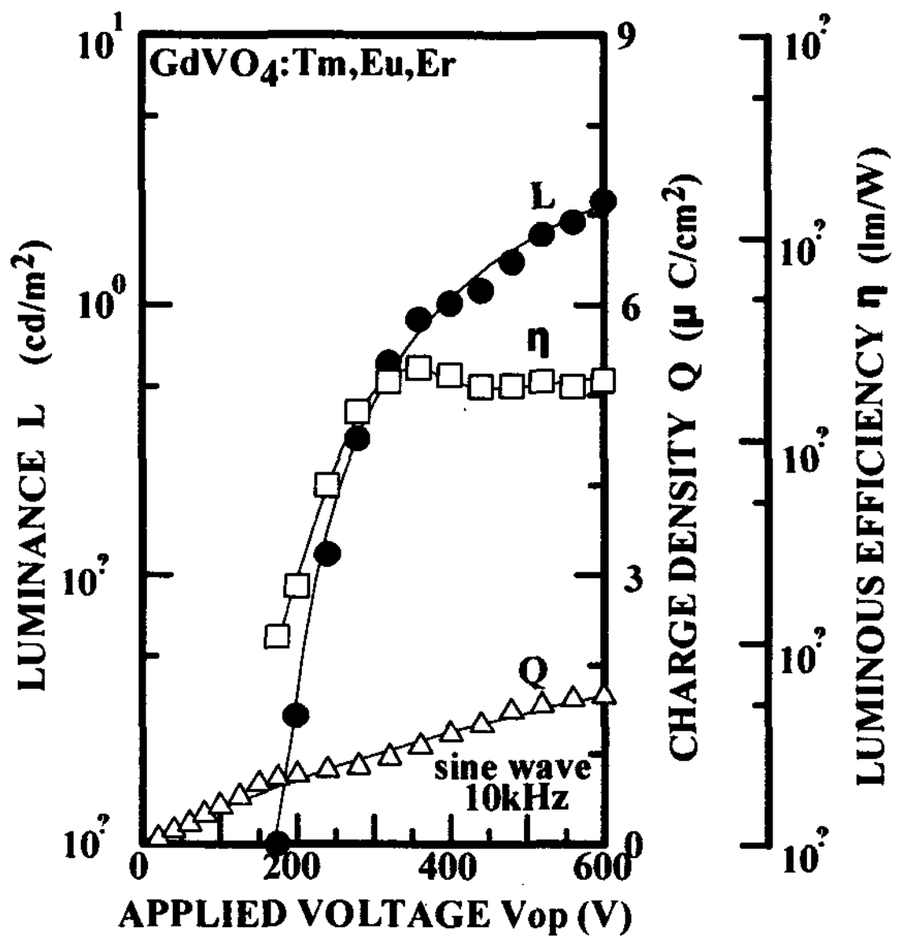

Fig. 9 L-V, Q-V and η-V characteristics of a $GdVO_4$:Eu,Er,Tm TFEL device driven at 10 kHz.

thin films co-doped with Eu, Er and Tm. As an example, Fig. 6 shows the PL emission spectrum of a white-emitting $GdVO_4$:Eu,Er,Tm phosphor thin film prepared with Eu, Er and Tm contents of 0.2, 0.7 and 1 at.%, respectively, and postannealed at 1000°C. As shown above in Figs. 1 and 3, the emission spectrum was not affected by the excitation wavelength when it was within the excitation spectrum. Figure 7 shows that the $GdVO_4$:Eu,Er,Tm thin film exhibited excellent white PL emission: CIE chromaticity color coordinates, (X=0.352 and Y=0.351).

A TFEL device fabricated with a $GdVO_4$:Eu,Er,Tm phosphor thin film as the emitting layer exhibited a white EL emission that was approximately the same as the white PL emission from the $GdVO_4$:Eu,Er,Tm phosphor thin film used as the emitting layer: Eu, Er and Tm contents of 0.2, 0.7 and 1 at.%, respectively. Figure 8 shows the EL emission spectrum for the $GdVO_4$:Eu,Er,Tm TFEL device: CIE chromaticity color coordinates, (X=0.351 and Y=0.381), also shown in Fig.7. In addition, luminance (L), transferred charge density (Q) and luminous efficiency (η) as functions of applied voltage (V) are shown in Fig. 9 for a $GdVO_4$:Eu,Er,Tm TFEL device driven by a sinusoidal wave voltage at 10 kHz. The color of EL emission observed from this TFEL device was white with an obtained maximum luminance of 3.2 cd/m^2. Although the obtained luminous efficiency in EL was relatively low, a high luminous efficiency in PL was attained in the white-emitting $GdVO_4$:Eu,Er,Tm thin film. The low luminous efficiency of TFEL devices may be explained by the difficulty of achieving impact excitation by hot electrons due to the large energy band-gap of the host material [2].

5. Conclusions

High-luminous efficiency full-color emitting $GdVO_4$ phosphor thin films co-doped with Eu, Er and Tm have been newly developed. The $GdVO_4$:Eu,Er,Tm phosphor thin films were first deposited on thick $BaTiO_3$ ceramic sheets by r.f. magnetron sputtering using powder targets and then postannealed at 1000°C in an air atmosphere. Full-color emissions in photoluminescence (PL) were obtained in $GdVO_4$:Eu,Er,Tm phosphor thin films prepared by varying the amount of Eu, Er and Tm. White PL emission was obtained in a $GdVO_4$:Eu,Er,Tm thin film with Eu, Er and Tm contents of 0.2, 0.7 and 1 at.%, respectively: CIE chromaticity color coordinates, (X=0.352 and Y=0.351). In addition, a luminance of 3.2 cd/m^2 in white emission was obtained in a thin-film electroluminescent device made with this thin film: driving voltage at 10 kHz.

Acknowledgments

The authors wish to acknowledge Mr. K. Tanida, K. Tomita, K. Wakahara and S. Watanabe for their technical assistance in the experiments. This work was partially supported by Grant-in Aid for Scientific Research No. 16560039 from Ministry of Education, Science and Culture of Japan.

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