Cathodoluminescence Enhancement of $CaTiO_3:Pr^{3+}$ by Ga Addition

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The phosphor $CaTiO_3:Pr^{3+}$ attracts much attention as a low-voltage red phosphor because of its good chromaticity and intrinsic conductivity. The addition of Ga into this $CaTiO_3:Pr$ led the luminance intensity to greatly enhance without the change of the wavelength for the electronic transition and the peak shape of it. The increase of the recombination rate of electron-hole pairs through the Ga ion doping, which was expected to play a role of a hole-trap center, is proposed to be one of the reasons for the enhancement of the cathodoluminescence intensity.

Key Words : Field emission displays (FED), Cathodoluminescence intensity, Phosphors

Introduction

Field emission displays (FEDs), one of promising flat panel displays, have to overcome many problems for the commercialization. Among them, the demand of low-voltage phosphors is a great challenging area in application of FEDs. The relatively low voltage operation of the anode plate results in easy build-up space charges at the surface of the phosphors and the low brightness due to the low voltage operation prevents an aluminum layer on the phosphor from being used.[1] On the other hand, since the conventional sulfide phosphors are known to deteriorate metal emitters of FEDs by the sulfur desorption from the anode plate,[2] the sulfide phosphors like ZnS with good brightness, unfortinutly, cannot be used. These limitations require developing and searching new oxide phosphor materials with good conductivity.

The $CaTiO_3:Pr$ phosphor is a low-voltage red phosphor with a good color quality and a good intrinsic conductivity. The host material, perovskite $CaTiO_3$, has a band gap energy of 3.7 eV,[3] which value is semiconductor-like and presents a good conductivity. The activator Pr^{3+} shows a number of different emission spectra depending on the host materials.[4,5] One of the relative intense emission lines in the emission spectra is the transition of red color from the $^1D_2$ level and the other is that of green color from the $^3P_0$ level. The usual host material including Pr^{3+} shows either only red or only green color, but there are host materials showing both of the colors. It is known that the $CaTiO_3:Pr$ phosphor shows only the red color. In this study, we investigated luminescence properties of the $CaTiO_3:Pr$ phosphor by the addition of Ga. It was found that the additive Ga caused the luminescence intensity to greatly enhance.

Experimental Section

Powder samples were prepared by conventional solid state reaction. The stoichiometric mixtures of $CaCO_3$, TiO_2, $Pr(NO_3)_3 \cdot 6H_2O$, Ga_2O_3 were firing at 1200 °C for 4 hrs.

The X-ray diffraction patterns were recorded using a MAC Science MXP 18 XRF diffractometer with Ni-filtered Cu Kα radiation (λ = 1.5406 Å) by step scanning (0.02°) in the 2θ range of 10°-80°.

The cathodoluminescence (CL) spectra were obtained using a demountable ultrahigh vacuum chamber equipped with in-house assembled CL spectrophotometer (ISS PC1). The adjustable electron beam (Kimball Physics, FRA-2X1-2/EGPS-2X1) is incident normal to the compacted powder specimen. The measurements were carried out with excitation voltage of 1 kV and the beam current density of 10 or 20 μA/cm^2.

Results and Discussion

The XRD patterns of the $CaTiO_3$ doped with various concentrations of Pr and Ga have been indexed orthorhombic symmetry. The cell parameters for $CaTiO_3:Pr$ are similar to that of $CaTiO_3$ due to the small size difference between Ca^{2+} and Pr^{3+} (r(Ca^{2+}) = 114 pm, r(Pr^{3+}) = 113 pm). In spite of difference in atomic radius of Ca and Ga (r(Ga^+) = 76 pm), the slightly increase of b parameter and slightly decrease of c parameter was observed in Ga doped $CaTiO_3:Pr$. So, it was found that the orthorhombic structure of $CaTiO_3:Pr$ was not disturbed by the addition of Pr and Ga.

The SEM images of $CaTiO_3:Pr$ show the particle size is increased with doping the Pr^{3+} ion. The particle size of $CaTiO_3:Pr$ is 2-3 μm. The $CaTiO_3:Pr$ have good crystallniity and round shape particles. The same phenomena are observed in Ga doped $CaTiO_3:Pr$. The particle size is increased with increasing Ga concentration. The particle size of Ga doped $CaTiO_3:Pr$ is ~3 μm. These facts implied that the dopant ions stabilized the structure of the host lattice, which increased the crystallinity and particle size of the $CaTiO_3$ phosphor.

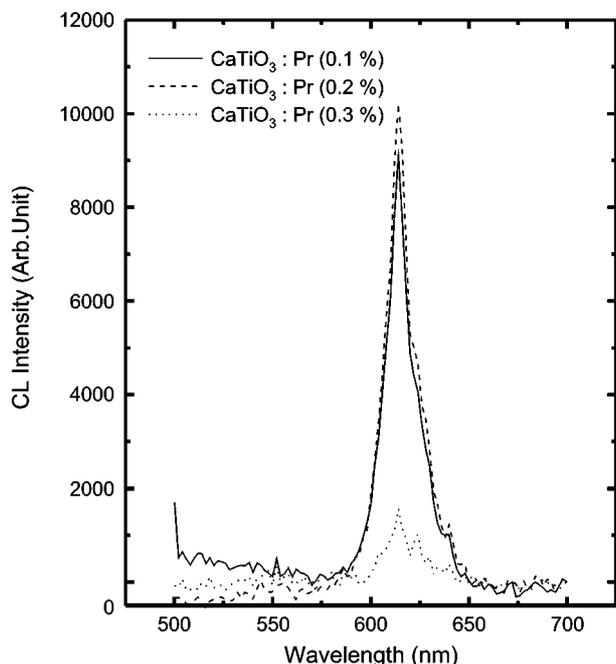Since the first report of the $CaTiO_3:Pr$ phosphor as a red phosphor,[6] some researchers tried to obtain the optimized

Figure 1. CL intensity of CaTiO₃:Pr with various Pr mole%. (anode voltage and current: 1 kV, 20 μA)

concentration of Pr for the maximum luminescence intensity.[7,8] Up to now, the optimized concentration of Pr has been known to be about 0.2 mole%. To examine this, we observed cathodoluminescence (CL) spectra with various Pr concentrations. Figure 1 shows the resulting CL spectra of CaTiO₃:Pr with various molar percentages of Pr. We obtained the maximum molar concentration of 0.1-0.2 mole% like the other reports. The peak position of the emission line was 614 nm which results from the transition
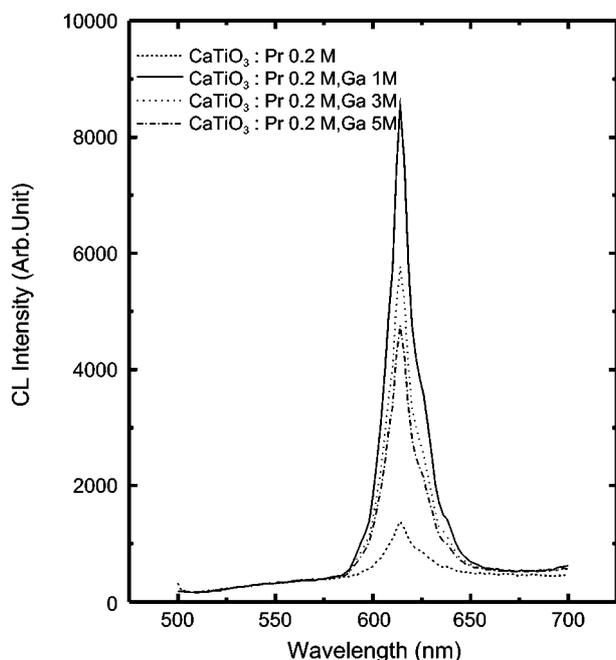

Figure 2. CL intensity of Ga(x)-doped CaTiO₃:Pr (x =1, 2 , 3 mole %). (anode voltage and current: 1 kV, 20 μA)

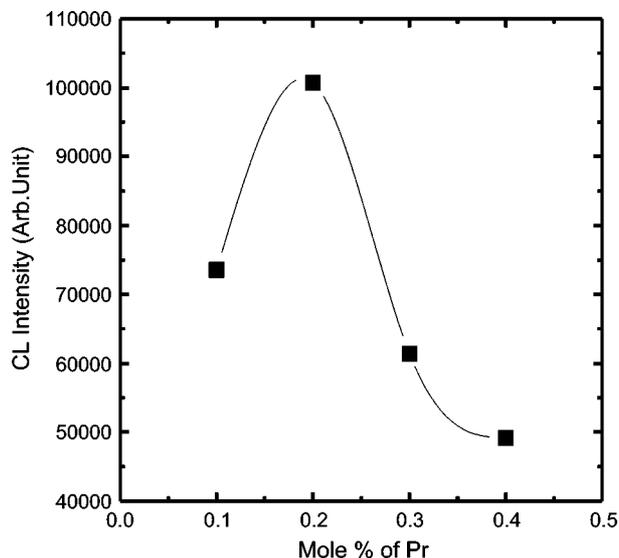**Figure 3**. Maximal peak CL intensity at 614 nm of CaTiO₃:Pr, Ga (1 mole %) with various Pr mole%. (anode voltage and current: 1 kV, 20 μA)

of $^1D_2 \rightarrow ^3H_4$, and other emission lines, for example a green line around 490 nm from $^3P_0 \rightarrow ^3H_4$, were not observed.

It was reported that the addition of monovalent ions to the CaTiO₃:Pr phosphor enhances the red emission intensity and the addition of Ga or Al to SrTiO₃:Pr does. However, the effect of the Ga addition to the CaTiO₃:Pr has not been reported. We substituted the Ti of the CaTiO₃:Pr (0.2 mole%) phosphor with Ga molar percentages of 1, 3, and 5 % and the resulting CL spectra are shown in Figure 2. In order to inquire into the effect of Ga doping, we also presented the spectrum of the CaTiO₃:Pr. Although the CL intensity decreases with increasing the addition of Ga, the maximal CL intensity at the Ga molar concentration of 1% is 8 times higher than that of CaTiO₃:Pr. Compared with the 60% enhancement of the intensity by the Ag⁺ addition,[7] we obtained even more remarkable enhancement of the CL intensity.

For the constant Ga molar %, the Pr concentration was varied. Figure 3 shows the CL peak intensity at 614 nm of CaTiO₃:Pr (x mole%), Ga (1 mole%) (x = 0.1-0.4). The maximal CL intensity was obtained at 0.2 mole% Pr, which shows the same trend as the CaTiO₃:Pr without Ga addition. So, according to our experimental results, the optimized Pr and Ga concentrations are 0.2 mole% and 1 mole%, respectively.

To examine the low-voltage luminescence characteristics, we tried changing the anode voltage. The CaTiO₃:Pr, Ga phosphor shows the more remarkable enhancement than the CaTiO₃:Pr phosphor (Fig. 4).

For the efficient red luminescence from Pr³⁺, the necessary condition is known that there is a low-lying 4f5d level, which plays a role of enhancing the non-radiative transition from $^3P_0$ to $^1D_2$. The non-radiative transition between the excited 4f states not only suppresses the green emission from $^3P_0$ to $^3H_4$, but also increases the population of the $^1D_2$ and so leads the red emission to enhance.[4,7] The Ga addition does
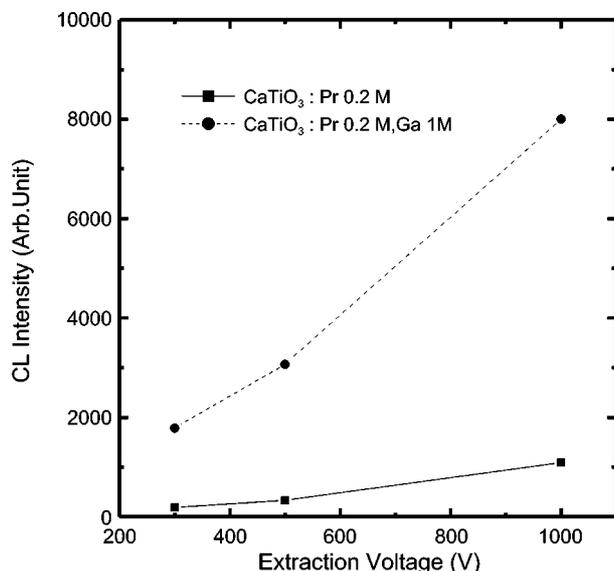
Figure 4. Maximal peak CL intensities at 614 nm of CaTiO₃:Pr (0.2%), Ga (1%) and CaTiO₃:Pr (0.2%) with various anode voltages. (anode current: 20 μA)

not have an effect on this process. Another important factor of the emission process is the band-to-band excitation. It corresponds to charge transfers from O(2p) states to Ti(3d) states or from Pr^{3+}(4f) to Ti(3d) states. Such a charge transfer usually produces electron-hole pairs and the photo-excitation of Pr^{3+} by the recombination process results in the population of the 4f excited levels of Pr. Therefore, the additive Ga ions play a role of hole trap centers and enhance the recombination rate of electron-hole pairs.

Conclusion

The Ga ion doping for Ti site in $CaTiO_3$:Pr^{3+} phosphors greatly enhanced cathodoluminescence intensity. By the doping of 1 mole % Ga ion, we obtained 8 times higher CL intensity than that of $CaTiO_3$:Pr^{3+}. The additive Ga ion is expected to play a role of a hole trap center and so enhance the recombination rate of electron-hole pairs. This process results in the population of the excited Pr^{3+} 4f levels and we can obtain remarkable enhanced red emission. The green emission from $^3P_0$ is greatly suppressed by the non-radiative transition through a low-lying 4f5d level.

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