

Mechanism for strong yellow emission of $Y_3Al_5O_{12}:Ce^{3+}$ phosphor under electron irradiation for the application to field emission backlight units

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This letter reports a strong yellow emission of $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) mixed with ZnS:Ag,Cl under electron excitation. The penetration depths of electron of 1 keV and photon of 2.7 eV in YAG:Ce were estimated to be approximately 1450 Å and 4.65 mm, respectively. Deeper penetration of blue light from ZnS:Ag,Cl helps to excite a larger number of Ce^{3+} in a mixture (ZnS:Ag,Cl + YAG:Ce), and YAG:Ce showed strong yellow emission via both cathodoluminescence and photoluminescence. The mixture showed the brightness of 120.5% compared to R,G,B phosphor mixture. This mixture of two phosphors was applied to a carbon nanotube field emission backlight unit. © 2007 American Institute of Physics. [DOI: 10.1063/1.2643064]

With the development of liquid crystal displays, the importance of backlight units (BLUs) has become large. In BLUs, the most common light generator is cold cathode fluorescent lamps (CCFLs). Light-emitting diodes (LEDs) are also quite commonly used for the same purpose.^{1,2} Recently, a planar light source using carbon nanotubes (CNTs) has been attempted with an intent to apply it for BLUs.³ In both cases of CCFL BLUs and LED BLUs, components such as diffuser and prism sheet are used, while they are not needed in field emission (FE)-BLUs using CNTs. CNT FE-BLUs can be fabricated using screen-printed CNT cathode and phosphor anode.⁴ White light is generated from a mixture of red, green, and blue (R,G,B) phosphors excited by electrons emitted from CNTs. However, when the mixture of R,G,B phosphors is used, each phosphor has a different degradation property so that, if possible, it is preferred to use a smaller number of phosphors.

To reduce the number of phosphors to be used in the anode of a CNT FE-BLU, it can be suggested that a yellow-emitting phosphor be used instead of both green-emitting and red-emitting phosphors. It is believed that there are few efficient yellow-emitting phosphors under irradiation of electron beam. However, in the case of $Y_3Al_5O_{12}:Ce$ (YAG:Ce), both cathodoluminescence (CL) and photoluminescence (PL) may occur simultaneously when YAG:Ce is mixed with a blue-emitting phosphor, since the PL excitation (PLE) band of YAG:Ce is located in a blue spectral region.⁵ Therefore, a stronger yellow emission can be expected.

In a similar attempt, Jung and Han reported improved CL in $Y_2SiO_5:Ce^{3+}-BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) mixed blue phosphor.⁶ However, they just mentioned the idea that PL could be added to CL of BAM without quantitative explanation for the mechanism of improved emission of BAM.

In this letter, we suggest a mechanism for the strong yellow emission of YAG:Ce through the calculation of penetration depths of electron emitted from CNTs and photon

emitted from ZnS:Ag,Cl, respectively. It will be shown that bright white light can be generated from a CNT FE-BLU using a two-phosphor system (ZnS:Ag,Cl and YAG:Ce).

A commercial ZnS:Ag,Cl and a synthesized YAG:Ce were used in the phosphor anode. The commercial ZnS:Ag,Cl was mixed with the synthesized YAG:Ce in the same volume ratio. The PL property of the synthesized YAG:Ce was optimized under 450 nm excitation because the reported CL efficiency of YAG:Ce is low and its PL efficiency is high under 450 nm excitation.^{7,8} To investigate the luminescent properties of the phosphors, PLE was characterized by a PL spectrometer (DARSA PRO 5100, PSI, Korea) using a xenon lamp (500 W) at room temperature. The CL study was performed with an electron beam of 1 keV and beam current density of $100 \mu A/cm^2$ using an electron gun system (FRA-2X1-2/EGPS-2X1, Kimball Physics). A CNT FE-BLU was fabricated with a multiwalled CNT cathode and a phosphor anode.

Figure 1 shows a PLE spectrum of YAG:Ce and a CL spectrum of ZnS:Ag,Cl. The broad excitation band of YAG:Ce is attributed to the allowed $4f \rightarrow 5d$ transition.⁵ Due to large crystal field splitting,⁹ the broad excitation band lies on a blue spectral region which corresponds to the emissive

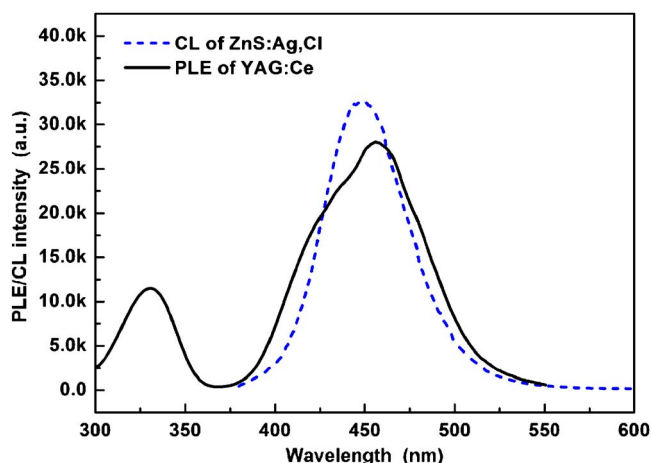


FIG. 1. (Color online) PLE spectrum of YAG:Ce and CL spectrum of ZnS:Ag,Cl.

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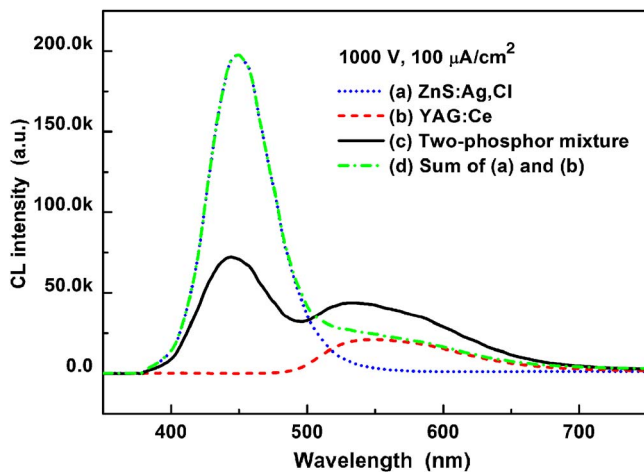


FIG. 2. (Color online) CL spectra of (a) ZnS:Ag,Cl, (b) YAG:Ce, (c) the mixture of two phosphors (ZnS:Ag,Cl+YAG:Ce), and (d) the sum of lines (a) and (b).

region of ZnS:Ag,Cl. According to Dexter,¹⁰ the spectral overlap is a very important factor for the energy transfer from energy donor (*D*) to energy acceptor (*A*). There are two kinds of energy transfer, i.e., nonradiative transfer and radiative transfer. Nonradiative energy transfer arises from multipolar interaction or exchange interaction. In the case of multipolar interaction, the critical distance for the energy transfer may be about 30 Å, and for the exchange interaction, the critical distance for the energy transfer may be 5–8 Å.¹¹ In this study, the energy donor and energy acceptor are located in different phosphor particles, and the distance between *D* and *A* is much larger than 30 Å. Moreover, since the spectral overlap consists of a considerable amount of overlap between an emission band and an allowed absorption band, there can be a considerable amount of radiative energy transfer. Since the PLE spectrum of YAG:Ce is similar to its absorption spectrum in the blue spectral region, one can know that spectral overlap is very large from Fig. 1. Therefore, it is believed that radiative energy transfer occurs from ZnS:Ag,Cl to YAG:Ce. A constant decay time of ZnS:Ag,Cl emission after mixing with YAG:Ce supports that the energy transfer is radiative. Since the CL efficiency of ZnS:Ag,Cl is high,¹² a strong blue light from ZnS:Ag,Cl can be an additional excitation source for YAG:Ce through the radiative energy transfer. Although the CL efficiency of YAG:Ce is low,⁵ it is expected that YAG:Ce can show a stronger yellow emission in a mixture of ZnS:Ag,Cl and YAG:Ce.

The intensity of the yellow light emitted from YAG:Ce depends on the number of emitted photons from it at a certain moment. If more photons are emitted from YAG:Ce at the same moment, the light intensity would be strong. Therefore, the PL and CL of YAG:Ce need to be involved simultaneously in order that more yellow photons should be emitted. Figure 2 shows the CL spectra of YAG:Ce, ZnS:Ag,Cl, and the mixture of ZnS:Ag,Cl and YAG:Ce, respectively. The CL spectrum of the mixed phosphor (ZnS:Ag,Cl + YAG:Ce) is line (c) and the sum of the CL spectra of YAG:Ce and ZnS:Ag,Cl is line (d). When line (c) was compared with line (d), the CL intensity of YAG:Ce in the mixed phosphor was stronger than the linear combination of the CL intensities of YAG:Ce and ZnS:Ag,Cl in the yellow spectral region. This means that the increased yellow emission is not due to the tail of the blue emission in the yellow spectral

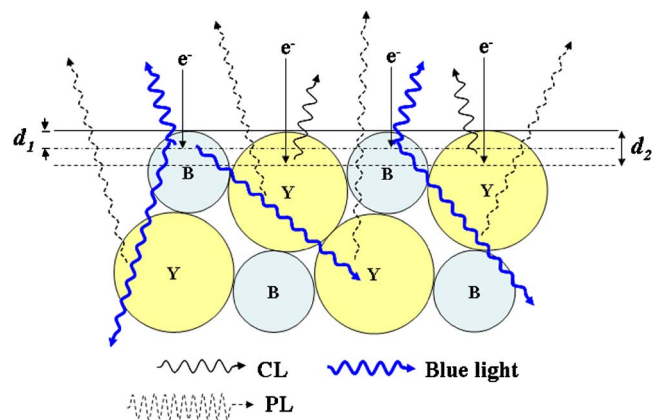


FIG. 3. (Color online) Schematic diagram of the mechanism for an enhancement of yellow emission in the mixture of ZnS:Ag,Cl and YAG:Ce.

region but due to an additional yellow emission from YAG:Ce. It also implies that PL and CL occurred simultaneously. When ZnS:Ag,Cl was mixed with YAG:Ce, the CL intensity of ZnS:Ag,Cl decreased as shown in Fig. 2. That indicates that the blue light emitted from ZnS:Ag,Cl was absorbed by YAG:Ce and radiative energy transfer occurred from ZnS:Ag,Cl to YAG:Ce.

Figure 3 shows the schematics of luminescent mechanism for enhancement of the yellow emission of YAG:Ce. In Fig. 3, “B” and “Y” represent blue-emitting ZnS:Ag,Cl and yellow-emitting YAG:Ce, respectively. In the range of 1–10 keV electrons in solid, the penetration depth of electrons into the phosphors is given as follows.¹³

$$R = 250 \left(\frac{A}{\rho} \right) \left(\frac{E_0}{Z_m^{1/2}} \right)^n, \quad (1)$$

where *A* is molecular weight, ρ is bulk density, Z_m is mean atomic number, $n = 1.2 / (1 - 0.29 \log Z_m)$, E_0 is excitation energy in units of keV, and *R* is penetration depth in units of Å. When the excitation energy of electron was 1 keV, the penetration depths of electrons into ZnS:Ag,Cl and YAG:Ce were estimated as approximately 220 and 1450 Å, respectively. In Fig. 3, d_1 (220 Å) and d_2 (1450 Å) indicate the penetration depths of electron beam in ZnS:Ag,Cl and YAG:Ce, respectively. Only ZnS:Ag,Cl and YAG:Ce crystallites within d_1 and d_2 are excited by electron beam and emit blue and yellow lights, respectively.

The penetration depth of the blue light into YAG:Ce can be obtained from the absorption coefficient of YAG:Ce. The intensity of light propagating in a medium decreases from its incident intensity at the surface by optical absorption and the intensity of the light at a distance *x* from the surface is given by Lambert’s law,¹⁴

$$I = I_0 e^{-\alpha x}, \quad (2)$$

where I_0 is the incident light intensity minus reflection loss at the surface and α is the absorption coefficient of a phosphor in units of cm^{-1} . From the measurement of absorption for YAG:Ce, α was calculated to be 2.153 cm^{-1} for the 452.5 nm blue light. From the value of α , the penetration depth of the blue light into YAG:Ce was obtained as about 4.65 mm which was much larger than that of electron. This result is in agreement with the fact that the penetration depth of radiation absorbed directly by activator ions is extremely large compared to the crystal size of the phosphors.¹²

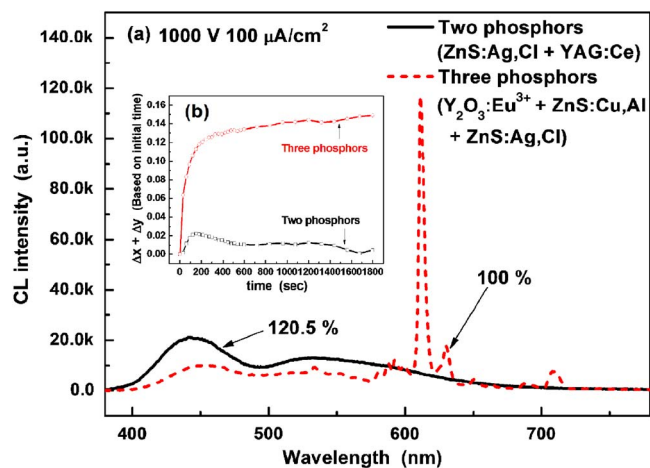


FIG. 4. (Color online) (a) CL spectra of the mixtures of two phosphors (ZnS:Ag,Cl+YAG:Ce) and three phosphors ($Y_2O_3:Eu^{3+}+ZnS:Cu,Al+ZnS:Ag,Cl$), respectively. The brightness was calculated using $\int_{380}^{780} I_{em}(\lambda)d\lambda$. (b) Variation of CIE coordinates of the mixture of two phosphors and three phosphors as a function of exposure time to electron beam.

Since the penetration depth of the blue light is much larger than that of electrons of 1 keV, YAG:Ce crystallites located deeper than d_2 are excited by blue light emitted from ZnS:Ag,Cl, and they emit the additional yellow light. In Fig. 3, the solid lines depict emissions by electron beam and the broken lines indicate the emission from YAG:Ce by the blue light. Consequently, the photoluminescent yellow emission is added to the cathodoluminescent one.

Figure 4(a) shows the CL spectra of the mixture of two phosphors (ZnS:Ag,Cl + YAG:Ce) and the mixture of three commercial phosphors (red-emitting $Y_2O_3:Eu^{3+}$ + green-emitting ZnS:Cu,Al + blue-emitting ZnS:Ag,Cl). The three-phosphor mixture was selected by considering the performance of P-22 phosphors and referring to Ref. 15. The brightness was compared to each other by integrating the CL intensity from 380 to 780 nm. When the brightness of the three-phosphor system is set to be 100%, the two-phosphor system showed a relative brightness of 120.5%. After employing the visual spectral sensitivity, the two-phosphor system showed a relative brightness of 109.0%. From this result, one can verify that a bright white light can be generated from the mixture of ZnS:Ag,Cl and YAG:Ce under irradiation of electron beam. In addition, the two-phosphor system showed stable color coordinates compared to the three-phosphor system. Figure 4(b) shows the difference (Δx , Δy) between the Commission Internationale de l'Éclairage (CIE) color coordinates at increasing exposure time and initial exposure time to the electron beam. The CIE color coordinates of the three-phosphor system changed severely after irradiation of electron beam for 30 min $[(x, y) = (0.32, 0.33) \rightarrow (0.39, 0.41)]$, while the CIE color coordinates of the two-phosphor system were relatively stable.

Figure 5 shows a photograph depicting an emission image of a 3.5 in. panel assembled using both a CNT cathode and a phosphor anode including YAG:Ce and ZnS:Ag,Cl. To operate a CNT FE-BLU, the prepared CNT FE-BLU was located inside a vacuum chamber. When it was driven at 1.5 kV, it showed a bright cool white light. Its brightness was about 1370 cd/m^2 and calculated luminous efficiency was about 6 lm/W. Its CIE color coordinates were (0.27,

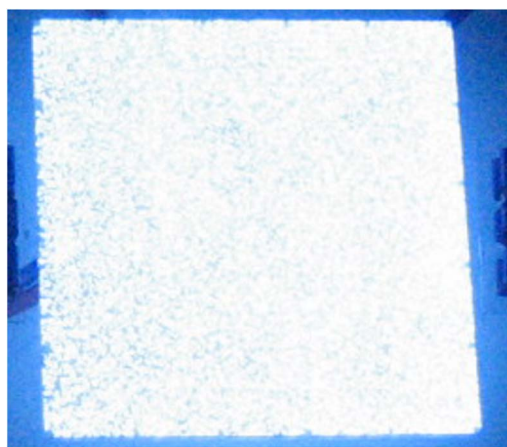


FIG. 5. (Color online) Image of a luminescent CNT FE-BLU. The applied voltage was 1.5 kV.

0.30) and color rendering index was 78. In the CNT FE-BLU, according to Eq. (1), the penetration depth of electron emitted from CNTs was calculated as approximately 3240 \AA which was still smaller than that of the blue light from ZnS:Ag,Cl. That is, when the mixture of ZnS:Ag,Cl and YAG:Ce was applied to a CNT FE-BLU, a bright white light can be realized via strong blue light from ZnS:Ag,Cl and stronger yellow light due to both PL and CL of YAG:Ce.

In conclusion, the yellow emission of YAG:Ce was enhanced by mixing it with the blue-emitting ZnS:Ag,Cl under irradiation of electron beam. Due to the deeper penetration of the blue light than electrons, a stronger yellow light was obtained from YAG:Ce in the two-phosphor mixture. When this mixture was applied to a CNT FE-BLU, it showed a bright cool white light. This study implies that if there is an efficient blue light source and the penetration depth of the blue light is larger than that of the primary excitation source, a bright white light can be realized by combining it with YAG:Ce whatever the primary excitation source is (e.g., electron, photon, and so on).

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