

## Cathodoluminescence Properties of In<sub>2</sub>O<sub>3</sub>-coated Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> Phosphors

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Europium-doped Y<sub>2</sub>O<sub>3</sub> phosphor (Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>) is a red phosphor that has been used in low-pressure fluorescence lamp, cathode ray tube (CRT) displays, and plasma display panels (PDPs) because of its characteristic sharp and hypersensitive luminescence.<sup>1-3</sup> Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> exhibits a charge transfer excitation peaking at 242 nm and produces a strong 610-nm emission from Eu<sup>3+</sup> with a narrow bandwidth attributed to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition.<sup>4-6</sup> The quantum yield of this emission varies from 60 to 74% depending on the porosity of the Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> particle.<sup>7</sup> Recently, this phosphor has attracted a great deal of attention for use in field emission displays (FEDs), since it is presumed to be inherently stable under electron beam excitation.<sup>8-12</sup> Most studies on the cathodoluminescence (CL) properties of Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> were conducted at accelerating voltages lower than 10 kV, although carbon nanotubes (CNTs), which are currently being investigated as electron field emitters for FEDs, require an applied voltage greater than 10 kV for reliable luminance.<sup>13,14</sup> Ntwacaborwa and co-workers<sup>15</sup> found that the CL intensity of Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> was significantly reduced by exposure to an electron beam. In contrast to the sulfide phosphors, Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> is an insulator with a bandgap energy of 6.0 eV. Electron irradiation of insulating materials builds a surface charge and creates a non-luminescent "dead layer" at the surface. Yamamoto and co-workers<sup>16</sup> found that the current must be increased to regain the desired CL intensity and that the emission appeared primarily at edges or rims of grooves or holes made on the phosphor screen. The surface of Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> can be coated with metal oxides, such as SiO<sub>2</sub>, MgO and Al<sub>2</sub>O<sub>3</sub> to alleviate this problem.<sup>17,18</sup> However, the CL data of Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> collected up to 4 kV showed that the resulting energy loss reduced the CL intensity. For FED applications, this problem can be solved by using a mixture of conductive materials such as In<sub>2</sub>O<sub>3</sub>, ZnO and SnO<sub>2</sub> with an insulating phosphor. For low-voltage FEDs, In<sub>2</sub>O<sub>3</sub> was found most effective in this regard.<sup>19,20</sup> In the current study, a Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> surface was coated with In<sub>2</sub>O<sub>3</sub> using two different deposition methods and the effects of the coating on the CL intensity was investigated as a function of accelerating voltages up to 17 kV. The findings revealed that the morphology of the In<sub>2</sub>O<sub>3</sub> coating played a key role in determining the CL intensity.

### Experimental

The In<sub>2</sub>O<sub>3</sub> coating was fabricated using a precursor solution composed of InCl<sub>3</sub> in ethanol or water. The phosphor was added to 50 mL of ethanol or 10 mL of water in which various

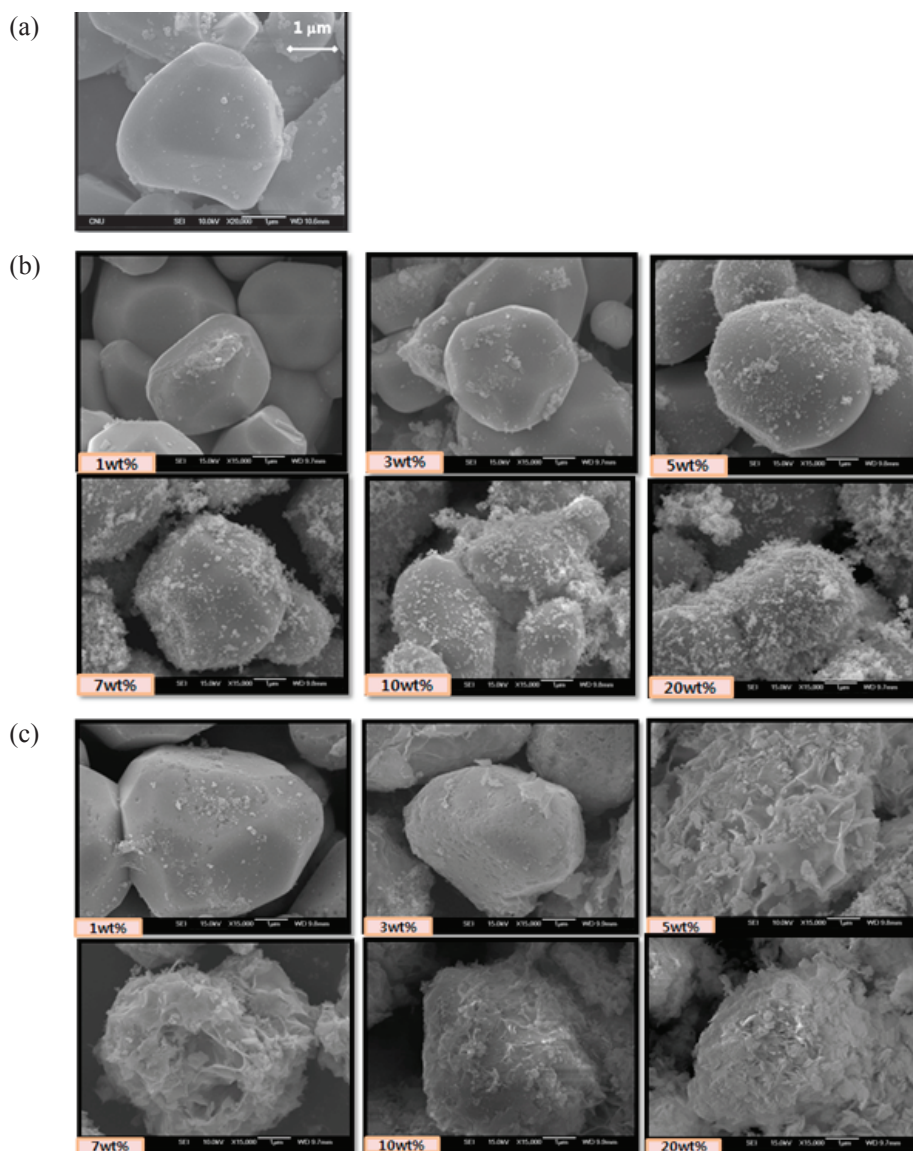
concentrations of InCl<sub>3</sub> had been dissolved. After adjusting to pH 10 with a NH<sub>4</sub>OH solution, the solutions were stirred for 1 h. The aqueous mixtures were heated at 70 °C to ensure the precipitation of In(OH)<sub>3</sub> onto the surface of the phosphor. The mixtures were then dried at 40 °C and heated in a box furnace at 400 °C for 3 h to convert indium hydroxide to indium oxide.

Phase information and surface morphology of the coated phosphors were determined by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). XRD data were collected on a D/Max-2000 diffractometer (Rigaku, Tokyo, Japan) with a graphite monochromator and Cu K $\alpha$  radiation ( $\lambda$  = 0.1541 nm). SEM micrographs and EDS spectra were acquired with a JSM-7000F FE-SEM (JEOL, Tokyo, Japan).

For the CL measurements, the uncoated and coated phosphors were deposited on glass using a screen printing method. A binder was prepared by dissolving ethyl cellulose (5 wt %) in  $\alpha$ -terpineol and heating at 70 ~ 80 °C for 2 h. The phosphors were mixed with the binder in 10:6 weight ratio and cast onto the glass surface using a YP-450HP printer (Yuil, Seoul, Korea). The cast phosphors were annealed applying a two-step heating process: 280 °C for 2 h and 460 °C for 1 h. The thickness of the cast phosphor layer was approximately 10  $\mu$ m. The CL intensity was measured with a BM-7 Luminance Colorimeter (Topcon, Japan) as a function of the electron acceleration voltage at a current density of 3  $\mu$ A cm<sup>-2</sup> under a high vacuum (5.0  $\times$  10<sup>-6</sup> torr) using an electron gun (PSI, Suwon, Korea). Photoluminescence (PL) spectra were also measured with an ARC 0.5 m Czerny-Turner monochromator equipped with a cooled Hamamatsu R-933-14 photomultiplier tube.

### Results and Discussion

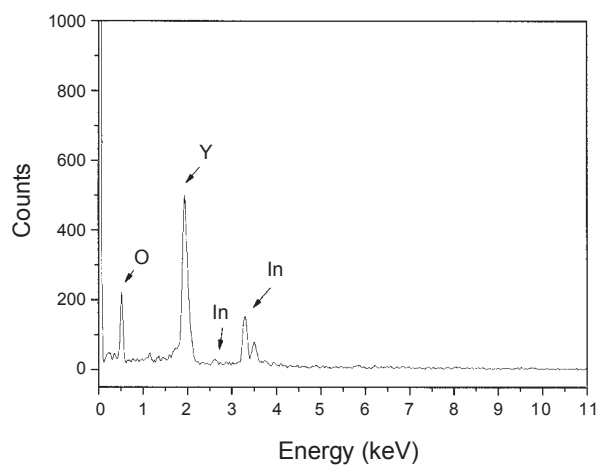
**Morphology and phase.** Fig. 1 shows the surface morphology of uncoated and In<sub>2</sub>O<sub>3</sub>-coated Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> after annealed at 400 °C for 2 h. With the exception of some adhered particles, the surface of the uncoated phosphor was smooth and clean. The surface morphology of the phosphor that had been treated with 1 and 3 wt % of InCl<sub>3</sub> in ethanol was almost the same as that of the untreated phosphor; i.e., no In<sub>2</sub>O<sub>3</sub> particles were apparent on the surface of the phosphor. Treatment with the 5 wt % In<sub>2</sub>O<sub>3</sub> resulted in partial coverage of the phosphor with In<sub>2</sub>O<sub>3</sub> nanoparticles. With increasing percentages of In<sub>2</sub>O<sub>3</sub>, the coverage of In<sub>2</sub>O<sub>3</sub> particles became denser, with complete coverage realized at 10 wt % InCl<sub>3</sub>. When aqueous solutions



**Figure 1.** FE-SEM images of (a) uncoated, and (b)  $\text{In}_2\text{O}_3$  nanoparticle- and (c)  $\text{In}_2\text{O}_3$  film-coated  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphors.

of  $\text{InCl}_3$  were used, the resulting morphology of  $\text{In}_2\text{O}_3$  coating differed from that observed with ethanolic solutions. In both solutions, the  $\text{In}_2\text{O}_3$  coatings were accomplished by the hydrolysis of  $\text{InCl}_3$  with  $\text{NH}_4\text{OH}$ . In the ethanolic solution, however, the polymerization *via* In-O-In network was very unfavorable, compared with the case in the aqueous solution. It might result in the nanoparticles instead of the film. As shown in Fig. 1, the surface of the phosphor was covered with a thin  $\text{In}_2\text{O}_3$  film after treatment with 3 wt %  $\text{InCl}_3$  in water. The thickness of the  $\text{In}_2\text{O}_3$  films increased with increasing percentages of  $\text{InCl}_3$ . These results demonstrated that the degree of  $\text{In}_2\text{O}_3$  coverage on the red phosphor was proportional to the amount of the  $\text{InCl}_3$  used in the deposition solution.

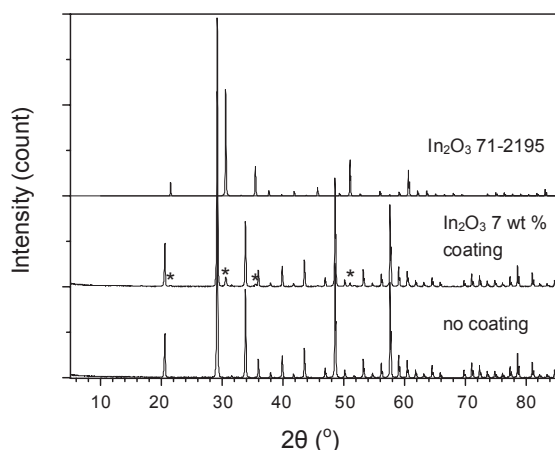
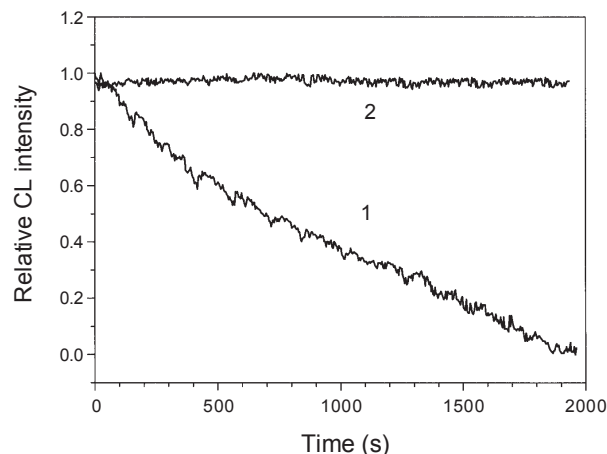
EDS spectrum was also measured to determine the relative surface composition of the  $\text{In}_2\text{O}_3$ -coated surface phosphors and it is shown in Fig. 2. The results of the compositions on the  $\text{In}_2\text{O}_3$ -coated phosphors are listed in Table 1. It can be found



**Figure 2.** EDS spectrum of typical  $\text{In}_2\text{O}_3$ -coated  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ .

**Table 1.** The element compositions of In<sub>2</sub>O<sub>3</sub>-coated phosphors from EDS analysis

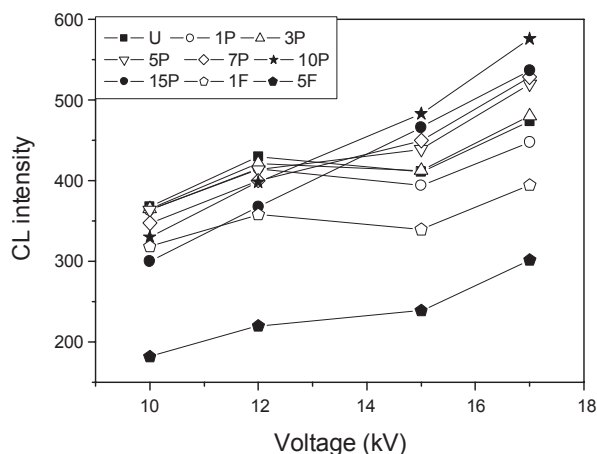
wt % Precursor	Nanoparticle (atomic %/wt %)			Film (atomic %/wt %)		
	O	Y	In	O	Y	In
1	74.2/33.75	24.43/61.79	0/0	77.6/38.4	22.4/61.7	0/0
3	78.6/39.7	21.1/59.1	0.34/1.23	76.7/37.2	23.3/62.8	0/0
5	76.0/35.8	22.3/58.4	1.7/5.8	79.5/40.8	19.4/55.3	1.1/3.9
7	71.8/31.0	26.2/62.8	2.0/6.2	77.3/37.5	20.9/56.3	1.8/6.1
10	73.2/32.1	23.3/56.6	3.6/11.3	79.8/40.9	18.5/52.8	1.7/6.3
15	78.0/37.7	17.6/47.3	4.4/15.1	77.4/36.9	18.5/49.1	4.1/14.0

**Figure 3.** XRD patterns of uncoated and In<sub>2</sub>O<sub>3</sub> nanoparticle-coated Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> phosphors (the lines of In<sub>2</sub>O<sub>3</sub> are noted by \*).**Figure 4.** Relative CL intensities of (1) uncoated and (2) In<sub>2</sub>O<sub>3</sub> nanoparticle-coated Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> phosphors. The concentration of the InCl<sub>3</sub> precursor solution was 10 wt %.

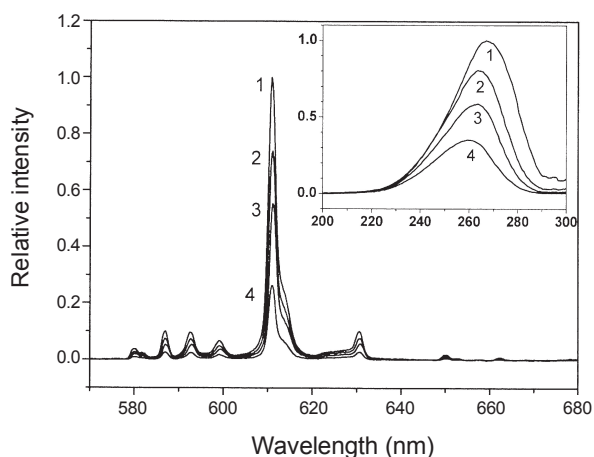
that the wt % composition of In increased with increasing the wt % of the precursor.

XRD patterns of both the uncoated and In<sub>2</sub>O<sub>3</sub> nanoparticle-coated phosphor are shown in Fig. 3. No In<sub>2</sub>O<sub>3</sub> peaks were detected with less than 3 wt % InCl<sub>3</sub> precursor. Above 3 wt % of InCl<sub>3</sub>, a characteristic peak of In<sub>2</sub>O<sub>3</sub> became discernible at  $2\theta = 30.6$ .

**CL properties.** Previously, Cho and co-workers<sup>8</sup> prepared a spherical Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> phosphor using an aerosol pyrolysis method and measured its CL intensity. The CL intensity of the uncoated Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> phosphor, when excited with an applied voltage of 400 V at a current density of 50  $\mu\text{A cm}^{-2}$ , decreased to 47% of the initial intensity after the first 10 min. In the current study, the aging of uncoated and the In<sub>2</sub>O<sub>3</sub>-coated Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> phosphor was evaluated during excitation at an accelerating voltage of 17 kV and 1.57  $\mu\text{A cm}^{-2}$ . As shown in Fig. 4, the CL intensity from the uncoated phosphor during high-energy electron bombardment decreased by 94% after 2000 s. In contrast, the phosphor that had been treated with 10 wt % of InCl<sub>3</sub> in ethanol maintained a stable CL intensity for the same 2000-s duration, despite the incomplete nanoparticle coverage. In the 10 ~ 17 kV (1.57  $\mu\text{A}$ ) excitation voltage range, as shown in Fig. 5, the CL intensity of the uncoated phosphor gradually increased with increasing voltage with some fluctuation in linearity. The CL intensity profiles of phosphors treated 1 and 3 wt % concentrations of InCl<sub>3</sub> were very similar to those of the uncoated phosphor. Above 3 wt %, however, the amount of fluctuation in the CL data decreased and the slope of the CL

**Figure 5.** CL intensities of uncoated and In<sub>2</sub>O<sub>3</sub> coated Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> phosphors measured in the high voltage range (U: uncoated, P: In<sub>2</sub>O<sub>3</sub> nanoparticle-coated, F: In<sub>2</sub>O<sub>3</sub> film-coated, digital: wt % InCl<sub>3</sub>).

intensity increased. At 10 kV, the CL intensity of the phosphor that had been coated with the 5 wt % solution of InCl<sub>3</sub> was almost equal to that of the uncoated phosphor. Increasing the voltage resulted in an increase in the relative CL intensity of the nanoparticle-coated phosphors. At 17 kV, the CL intensity of the coated phosphors increased by more than 10%. Phosphors treated with InCl<sub>3</sub> solutions above 7 wt % exhibited lower CL intensity than the un-coated phosphor at voltages up to 12 kV.



**Figure 6.** Luminescence spectra of uncoated and nanoparticle  $\text{In}_2\text{O}_3$ -coated  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  excited at 264 nm (1: uncoated, 2: 1 wt %, 3: 3 wt %, 4: 5 wt %  $\text{InCl}_3$ ). The strongest band at 610.8 nm corresponds to the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions. Charge-transfer excitation bands for the 610.8 nm emissions from the uncoated and coated phosphors are inserted.

At 17 kV, however, the CL intensity increased substantially. The strongest CL intensity was observed at 17 kV with a phosphor that had been treated with the 10 wt %  $\text{InCl}_3$  solution, representing a 22% enhancement over the CL of the uncoated phosphor. The CL intensities as a function of applied voltage for the 5, 7, 10 and 15 wt % coated phosphors were evaluated as  $20.2 (\pm 4.1)$ ,  $24.4 (\pm 2.9)$ ,  $34.0 (\pm 2.4)$  and  $33.6 (\pm 0.3)$   $\text{Cd m}^{-2} \text{V}^{-1}$ , respectively. Fig. 5 shows that the CL intensity of phosphors coated with  $\text{In}_2\text{O}_3$  films resulting from the aqueous deposition of  $\text{InCl}_3$  was significantly less than that of the uncoated phosphor. For the phosphor treated with 1 wt %  $\text{InCl}_3$ , the SEM image shows that only a small fraction of the surface was covered by the  $\text{In}_2\text{O}_3$  film. However, this slight coverage was enough to reduce the CL intensity by about 13%.

The nanoparticle  $\text{In}_2\text{O}_3$ -coating effect on the CL intensity is very extraordinary, compared with the case for the PL. Fig. 6 shows the PL spectra of uncoated and the nanoparticle  $\text{In}_2\text{O}_3$ -coated  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphor, excited by the charge-transfer band ( $\lambda_{\text{exc}} = 264$  nm). The PL intensity of the coated phosphor was significantly affected by the  $\text{In}_2\text{O}_3$  nanoparticles: the PL intensity significantly decreased with increasing the amount of the  $\text{In}_2\text{O}_3$  nanoparticles. For the electron-beam excitation, the  $\text{In}_2\text{O}_3$  nanoparticles were very effective in reducing charge buildup on the surface of the insulating phosphor during high-voltage excitation to result in the beam penetrating into the deep inside of the phosphor.

### Conclusions

A red phosphor composed of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  was coated with  $\text{In}_2\text{O}_3$  by immersing the phosphor into either an ethanol or aqueous solution of  $\text{InCl}_3$  precursor with subsequent heat annealing. The morphology of the coating depended on the solvent used

in the precursor solution. Precursor deposition from ethanol resulted in partial coverage of the phosphor surface by  $\text{In}_2\text{O}_3$  nanoparticles; the use of an aqueous solution resulted in multi-layered  $\text{In}_2\text{O}_3$  thin films. Aging effects of the uncoated phosphor during excitation were profound; the CL intensity decreased by about 94% after 2000 s, presumably due to surface charging of the phosphor induced by high-energy electron bombardment. The CL intensity of both uncoated and coated phosphors was measured at excitation voltages between 10 and 17 kV. The  $\text{In}_2\text{O}_3$  nanoparticles were very effective at stabilizing and enhancing the CL intensity, even at sub-monolayer coverage. In contrast, thin film coatings of  $\text{In}_2\text{O}_3$  significantly reduced the CL intensity. From these results, the conclusion was drawn that surface modification of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  with  $\text{In}_2\text{O}_3$  nanoparticles would significantly improve the luminance of FEDs operating at voltages above 10 kV.

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