Abnormal reduction of Eu ions and luminescence in CaB$_2$O$_4$: Eu thin films

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Thin films of CaB$_2$O$_4$: Eu were deposited on glass substrates by spray pyrolysis. The abnormal reduction of Eu^{3+} to Eu^{2+} in as-grown thin films was found at the growth temperatures from 300 to 500 °C. Blue cathodoluminescence was observed by annealing films in air, correlating with further abnormal reduction of Eu ions and crystallization of compounds. These phenomena were explained by an electron transfer mechanism. The chromaticity coordinates were $x=0.193$ and $y=0.089$ with a dominant wavelength of 455 nm. Our results indicate calcium borate doped with Eu is a blue phosphor at temperatures suitable for the use of glass substrates in flat panel applications. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1808876]

Selection of blue phosphors for the anode is becoming more critical since field emission display (FED) is now being produced. The most efficient blue phosphors currently available are metal sulfides,[1–3] such as ZnS: Ag: Cl (P22B). Although they possess excellent luminescence properties, the lifetime of the display is limited by the degradation of these sulfide phosphors during operation. Oxide-based hosts may emerge as an alternate choice for the blue phosphor, due to their superior chemical and thermal stability. The most oxide blue phosphors currently available include Y$_2$SiO$_5$: Ce and Sr$_2$CeO$_4$.[4–7] Eu^{2+}-doped phosphor is a promising blue phosphor. However, Eu^{2+} is unstable in an oxidizing atmosphere, and it can be oxidized to Eu^{3+} easily via Eu$^{2+}\rightarrow$Eu^{3+}+e. Many researchers have attempted to find host materials that stabilize Eu^{2+}, such as flfuroaluminate glasses, BaMgAl$_{10}$O$_{17}$ and ZnS nanoparticles.[8–11] Annealing those phosphors at relative high temperatures for hours in a reducing atmosphere is generally required for both crystallization of compounds and reduction of Eu^{3+} to Eu^{2+}. Unfortunately, those processes are not suitable for the use of glass substrates in flat panel applications. Also, it is not a convenient method to use reducing atmosphere in large-scale production because of the added safety requirements. Recently, we reported the use of spray pyrolysis to deposit thin films of borates.[12,13] Blue cathodoluminescence (CL) characteristics were presented by activating thin films in air at temperatures suitable for glass substrates. However, previously reported thin-film phosphors exhibit blue emission bands that peak at 416 and 425 nm for Ba$_2$B$_5$O$_9$Cl: Eu and Sr$_2$B$_5$O$_9$Cl: Eu, respectively. Thus, the blue emission of borates available at the present time is deeper as compared to conventional blue phosphors, which does not completely satisfy the requirement of FED. Since blue lines depend on the crystal property of the host matrix, it is possible to tune the material for specific emitting spectra. In this letter, we report borate materials, CaB$_2$O$_4$: Eu by using spray pyrolysis of aqueous solutions. The phosphor had a better chromaticity with its maximum peak at 445 nm.

Thin films of CaB$_2$O$_4$ doped with 2.0 at. % Eu were prepared using spray pyrolysis of an aqueous solution containing Ca(OOCCH$_3$)$_2$, H$_3$BO$_3$ and Eu(OOCCH$_3$)$_3$. Excess H$_3$BO$_3$ was used in the precursor solution. The Corning 7059 glass substrates were used in our deposition. The spray was developed by an ultrasonic nebulizer and was directed towards the substrate by a carrier gas of humid air. The spray chamber was mounted on an *x-y* translation table to raster the aerosol across the substrate surface. After deposition, some thin films were annealed either at 800 °C for 2 min in air by using a homemade rapid thermal annealing system, or at 630 °C for 1 h in a tube furnace. The typical thickness of the films was 1.3 μm using a surface profile measuring system. The crystal structure determination and phase identification of the films were investigated by x-ray diffraction (XRD) technique. The CL was obtained using a CL luminoscope (Relion Industries ELM-2B). Luminescence spectra were measured using an Ocean Optics S2000 charge coupled device spectrometer (350–900 nm). A Minolta T-1M illuminance meter was used to determine the luminance of the films.

Figure 1 shows the XRD spectra for thin films of CaB$_2$O$_4$: Eu. Figure 1(a) illustrates that the as-grown film deposited at 300 °C was apparently amorphous or consisted of very small crystallites. The films annealed at 630 °C for
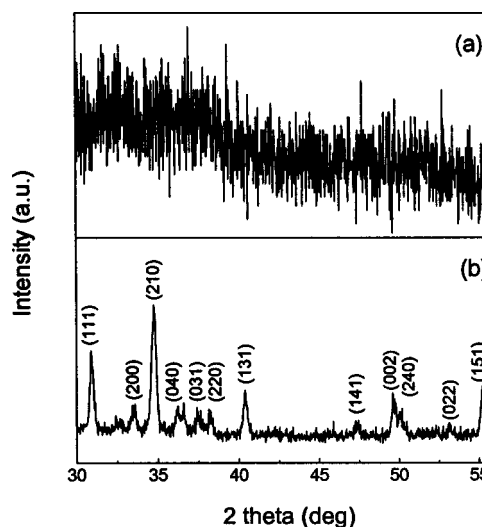

FIG. 1. XRD patterns for CaB$_2$O$_4$: Eu thin films grown on glass substrates: (a) as-grown at 300 °C, (b) deposited at 300 °C and annealed at 630 °C for 1 h.

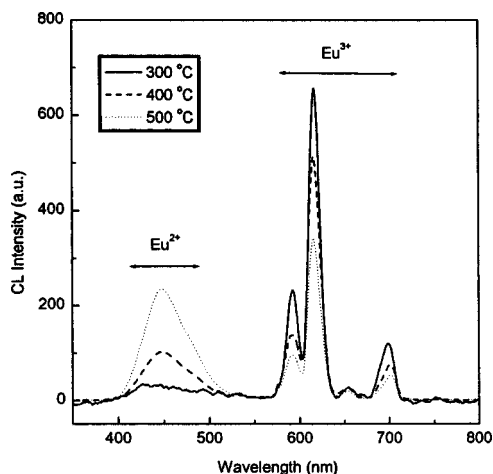[a]Author to whom correspondence should be addressed; electronic mail: jhhao@hku.hk

FIG. 2. CL spectra for the as-grown films of CaB_2O_4: Eu deposited at 300, 400, and 500 °C.

1 h [Fig. 1(b)] formed a polycrystalline structure. All diffraction peaks of XRD agreed well with CaB_2O_4 having orthorhombic structure ($a=6.22, b=11.61, c=4.28$).

Figure 2 shows the CL spectra of the as-grown films deposited between 300 and 500 °C. A 5 kV excitation voltage was used for CL measurement at room temperature. The current density on the sample was measured to be 62 $\mu A/cm^2$ for beam current of 0.5 mA. The coexistence of CL spectra corresponding to transitions for both Eu^{3+} and Eu^{2+} was observed for the as-grown films deposited from 300 to 500 °C. As the growth temperature increased, more amount of emission due to the transition of Eu^{3+} changed into a single peak around 445 nm, corresponding to electronic energy levels of Eu^{2+} ions.

Figure 3 shows the CL spectra of the films deposited at 300 °C, and then annealed either at 630 °C for 1 h [Figs. 3(a) and 3(b)] or at 800 °C for 2 min [Fig. 3(c)]. The film annealed at 630 °C had a single emission with the maximum at about 445 nm (due to $d \rightarrow f$ transition of Eu^{2+}) along with
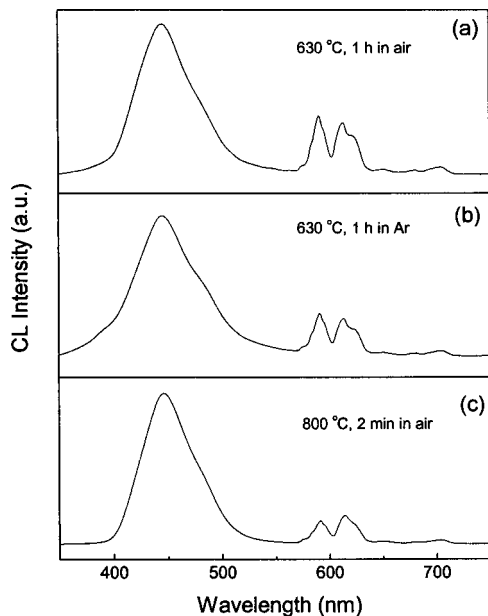

FIG. 3. CL spectra for the films of CaB_2O_4: Eu deposited at 300 °C, and then annealed (a) in air at 630 °C for 1 h, (b) in Ar ambient at 630 °C for 1 h, (c) in air at 800 °C for 2 min.

weak emissions due to Eu^{3+}. Thus, a majority of the europium was converted from a 3+ to a 2+ valency even though the film was annealed in air. In addition, there are no large differences in the CL spectra of the films annealed in air and Ar ambient as shown in Figs. 3(a) and 3(b). It indicates that the oxidation of Eu ions of annealed film in air was not apparent. For the film rapid annealed at 800 °C, the single emission centered at 445 nm was more intense and the weak emissions due to transitions of Eu^{3+} decreased. These results exhibited that the amount of Eu^{3+} reduced to Eu^{2+} increased as the activated temperature was increased. On the other hand, the conversion from Eu^{3+} to Eu^{2+} may be related to the structure change of the thin films in view of the XRD results in Fig. 1. The crystallization of the films changed from amorphous to polycrystalline structure would be helpful to the quenching of the emission at 593, 616, and 698 nm and enhancement of the emission at 445 nm.

It is unusual that the reduction of Eu^{3+} ions could occur even for the as-grown films deposited between 300 and 500 °C as shown in Fig. 2, and a majority of the europium was converted from a 3+ to a 2+ valency for the films annealed in air at temperatures suitable for the use of glass substrates as shown in Fig. 3. Previous studies indicated that the rigid three-dimensional network of BO_4 tetrahedra is necessary to stabilize the divalent rare earth ions in an oxidizing atmosphere.[14–16] In the case of CaB_2O_4: Eu, the Ca^{2+} ions were replaced by the Eu^{3+} ions when trivalent Eu^{3+} ions were doped. To keep the electroneutrality of the compound, the replacement of three Ca^{2+} ions by only two Eu^{3+} ions could occur. A negative Ca^{2+} vacancy was formed and may act as a donor of electrons. Thus, the abnormal reduction was attributed to an electron transfer from this defect to Eu^{3+} by thermal stimulation. According to the model, we might infer that the more electrons carried by negative vacancies were created, the more Eu^{3+} ions would be reduced in compounds. The mechanism was further supported by those reported co-doping experimental results.[17,18] In their studies, the intensity of the luminescence of Eu^{2+} was found to increase when Tb^{3+} was incorporated in SrB_4O_7: Eu phosphor. The phenomena can be explained with electron transfer theory. The Eu^{3+} ($4f^6$) ion tends to obtain an electron to get its electronic configuration ($4f^7$) and Tb^{3+} ($4f^8$) ion lose an electron in order to get its electronic configuration ($4f^7$). Eu^{3+} and Tb^{3+} ions are a pair of conjugate rare earth ions. When they are co-doped in borate matrix, they can transfer an electron from Tb^{3+} to Eu^{3+} ion to get their half filled $4f$ shells configuration ($4f^7$). Similar mechanism may be applicable to our present observation. In our case, the negative Ca^{2+} vacancy of CaB_2O_4: Eu could play similar roles to the Tb^{3+} ion incorporated in SrB_4O_7: Eu phosphor.

Usually the emission bands of Eu^{2+} due to $4f^7 \rightarrow 4f^65d^1$ transition are sensitive to the nature of host materials. The single bands with the maximum at 445 nm in Fig. 2 and 3 indicate that the Eu^{2+} might be located in one lattice site in CaB_2O_4: Eu. Compared with earlier studies on other alkaline earth element (Sr etc.) borate-based hosts,[14] the results are also indicative that the cation structures of borates have an influence on the transfer process of the defect electrons to the Eu^{3+} ions. This influence of the cation type on the emission band change is likely due to a crystal field effect.[19] As the radius of the alkaline earth ion decreases, the crystal field splitting of the $5d$ level becomes larger. Consequently, a larger crystal field splitting will shift the lowest
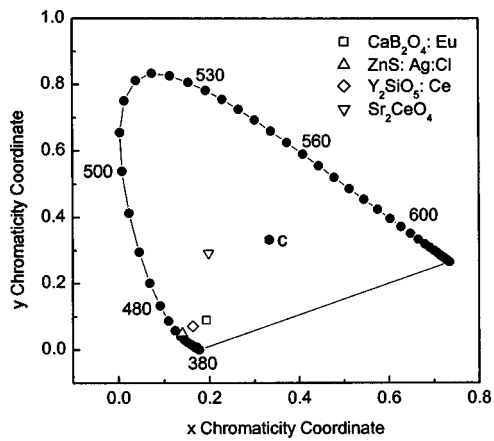
FIG. 4. A CIE chromaticity diagram showing the chromaticity points of the annealed CaB$_2$O$_4$: Eu thin films. For comparison, the chromaticity points of ZnS: Ag: Cl, Sr$_2$CeO$_4$ and Y$_2$SiO$_5$: Ce phosphors are also shown (from Refs. 1, 5, and 7).

$4f^65d$ state to lower energies. Because of this effect, a change in type of cation in borate compounds may alter the peak wavelength of the blue emission.

The location of the color coordinates of annealed films of CaB$_2$O$_4$: Eu on the CIE chromaticity diagram is presented in Fig. 4. The chromaticity coordinates were x =0.193 and y=0.089 with a dominant wavelength of 455 nm and a purity of 78%. For comparison, the standard blue phosphor, ZnS: Ag: Cl powder,[1] and oxide blue phosphors, such as Sr$_2$CeO$_4$ and Y$_2$SiO$_5$: Ce powders are also shown in Fig. 4.[5,7] Consequently, our annealed films are comparable to the standard blue phosphor and Y$_2$SiO$_5$: Ce in terms of dominant wavelength, although the improvement of color purity is required. Additionally, the coordinates of our blue phosphor are better than those of Sr$_2$CeO$_4$.

In summary, thin-film blue phosphors of CaB$_2$O$_4$: Eu were first prepared on glass substrates using spray pyrolysis of an aqueous solution. Films activated in air exhibited blue CL, due to the abnormal reduction of Eu^{3+}→Eu^{2+}. The chromaticity coordinates for the annealed films are comparable to those of the blue phosphors currently available.

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