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Tuning of the blue emission from europium-doped alkaline earth chloroborate thin films activated in air

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Thin films of $M_2B_5O_9Cl:Eu$ ($M=Ca, Sr, Ba$) were prepared on glass substrates using spray pyrolysis. Blue cathodoluminescence due to the abnormal reduction of $Eu^{3+} \rightarrow Eu^{2+}$ was obtained by annealing films in air. The cation of the host lattice was found to affect the effectiveness of the reduction process, which could result in influencing the emission band. By selecting types and composition of alkaline cation, it was possible to tune the dominant emitting wavelength between 435 to 465 nm. Activation of the films occurred at temperatures suitable for the use of glass substrates. © 2003 American Institute of Physics. [DOI: 10.1063/1.1569048]

Blue luminescent properties have been of great interest for applications in flat-panel displays and optoelectronic devices.¹⁻³ Selection of the emitting wavelength is required to meet requirements of some applications.^{2,4} Recently, development of oxide-based phosphors has received considerable attention due to their superior chemical and thermal stability. Some researchers⁵⁻⁸ have demonstrated the blue luminescent characteristics from alkaline earth element (Sr, etc.) oxide-based hosts, such as Sr_2CeO_5 and $Sr_2Al_5O_{25}$. In addition, our earlier work^{9,10} showed that thin films of Eu-doped $Sr_2B_5O_9Cl$ and $Ba_2B_5O_9Cl$ had excellent chromaticity coordinates for blue phosphors. However, these phosphors exhibit blue specific to hosts and the dopants. There seems to be no report concerning the systematic adjustment of blue emission of oxide thin-film phosphors. In this letter, we report the tuning of the blue emission by changing cation type and composition in $M_2B_5O_9Cl:Eu$ ($M=Ca, Sr, Ba$). Spray pyrolysis was used to deposit these thin films because it has some advantages over vacuum deposition in terms of tailoring materials composition and large-scale deposition. In particular, all blue phosphors in this work were activated in air at temperatures suitable for glass substrates, which are used in a number of applications, such as field-emission displays.

Thin films of $M_2B_5O_9Cl$ ($M=Ca, Sr, Ba$) doped with 2.0 at. % Eu were prepared using spray pyrolysis of an aqueous solution containing MCl_2 , H_3BO_3 , and $Eu(OOCCH_3)_3$. Excess H_3BO_3 was used in the precursor solution to compensate evaporation. The spray system was described in detail elsewhere.^{11,12} The Corning 7059 glass substrates used in our deposition had annealing and softening points of 639 and 844 °C, respectively. The typical thickness of the film was around 1.2 μm . After deposition, thin films were annealed either at 800 °C for 2 min in air by using a home-made rapid thermal annealing system, or at 630 °C for 1 h in a tube-furnace. The cathodoluminescence (CL) and luminance measurements were as described earlier.^{9,10}

Some of thin films were examined using x-ray diffraction techniques.^{9,10} Usually, as-grown films were apparently amorphous or consisted of very small crystallites. Annealed films formed a polycrystalline structure of $M_2B_5O_9Cl:Eu$. Scanning electron microscopy supported the conclusion.¹³

For the as-grown films of $M_2B_5O_9Cl:Eu$ deposited at 450 °C, Fig. 1(a) shows the CL spectra at room temperature using a 5 kV excitation voltage. The current density on the sample was measured to be 62 $\mu A/cm^2$ for beam current of

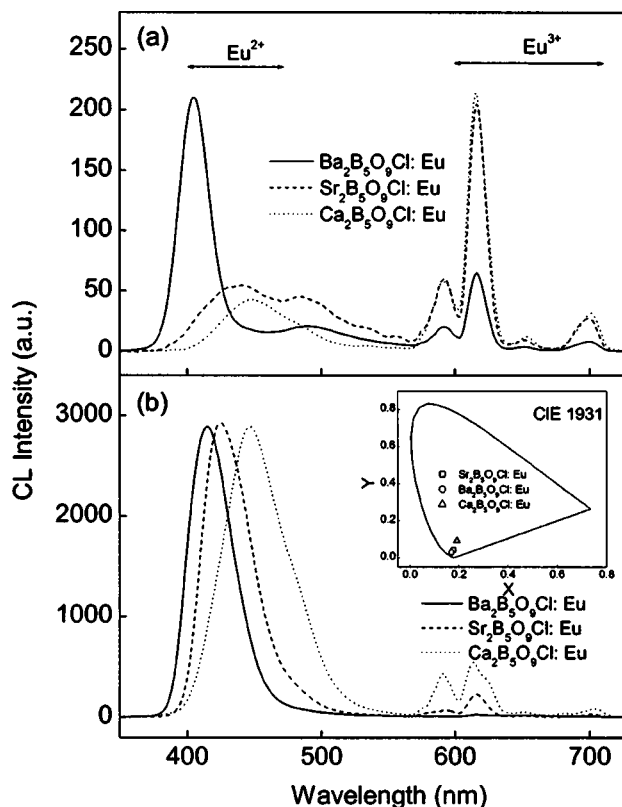


FIG. 1. CL for thin films of $M_2B_5O_9Cl$ ($M=Ca, Sr, Ba$) doped with 2% Eu: (a) as-grown at 450 °C; and (b) deposited at 450 °C and annealed at 800 °C for 2 min in air. A CIE chromaticity diagram showing the chromaticity points of each film is presented in inset.

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TABLE I. Peak wavelength λ_{peak} , FWHM of CL spectra, chromaticity coordinates CIE, dominant wavelength λ_{domin} , and color purity compared to CIE Standard Source C for the CL of annealed films of $M_2B_5O_9Cl:Eu$ ($M = Ba, Sr, Ca$) and three mixed systems.

Materials	λ_{peak} (nm)	FWHM (nm)	CIE (x, y)	λ_{domin} (nm)	Color Purity (%)
$Ba_2B_5O_9Cl:Eu$	416	38	(0.171, 0.029)	435	95
$Sr_2B_5O_9Cl:Eu$	425	42	(0.179, 0.044)	445	90
$Ca_2B_5O_9Cl:Eu$	448	58	(0.193, 0.099)	465	77
$(Sr, Ca)B_5O_9Cl:Eu$	439	49	(0.169, 0.054)	455	89
$(Ba, Ca)B_5O_9Cl:Eu$	434	60	(0.207, 0.101)	450	73
$(Sr, Ba)B_5O_9Cl:Eu$	421	38	(0.209, 0.092)	440	75

0.5 mA. The coexistence of CL spectra corresponding to transitions for both Eu^{3+} and Eu^{2+} was observed for all compounds. The amount of emission due to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} followed the sequence of $Ba > Sr > Ca$. It is consistent with our previous studies on $Ba_2B_5O_9Cl:Eu$,¹⁰ which have showed that the reduction of Eu^{3+} ions in $Ba_2B_5O_9Cl:Eu$ could occur at temperatures as low as 140 °C. Eu^{3+} was found to be reduced to Eu^{2+} more efficiently in thin films of $Ba_2B_5O_9Cl$. These results exhibit that the amount of Eu^{3+} reduced to Eu^{2+} increased when the ionic radius of the alkaline earth in the host was increased, indicating that the cation structures of borates have an influence on the electron transfer. Moreover, $Ba_2B_5O_9Cl:Eu$ exhibited a relatively sharp peak due to the Eu^{2+} transition whereas $Ca_2B_5O_9Cl:Eu$ and $Sr_2B_5O_9Cl:Eu$ phosphors exhibited either a broad band or multibands. The single bands indicate that the Eu^{2+} might be located in one lattice site in $Ba_2B_5O_9Cl:Eu$ and $Ca_2B_5O_9Cl:Eu$, and multibands indicate that Eu^{2+} ion probably occupied more than one kind of center in the crystal.

Figure 1(b) shows the CL spectra of the compounds deposited at 450 °C, and then annealed at 800 °C for 2 min in air. Similar CL spectra were obtained for the films annealed at 630 °C for 1 h. These spectra had an intense single sharp peak in the blue region along with weak peaks due to Eu^{3+} for each compound. The location of the color coordinates of each film on the CIE chromaticity diagram is presented in inset of Fig. 1(b). Table I lists peak wavelength, full width at half maximum (FWHM) of main peaks, chromaticity coordinates, dominant wavelength, and color purity compared to CIE Standard Source C for CL spectra of each annealed film. Obviously, the emission band shifts to longer wavelength and FWHM increases with decreasing ionic radius of the cation, that is, in the order $Ba > Sr > Ca$. Peters and Baglio¹⁴ did pioneering work on the structural and luminescent properties of single-crystal alkaline earth chloroborates activated with europium. The results presented in Fig. 1 and Table I are in reasonable agreement with their data. However, our polycrystalline films had FWHM about 12–18 nm larger than those of the single-crystal samples, indicating that crystallinity and/or grain boundaries can affect luminescence features. Our data are also similar to those reported for powder samples of $M_2B_5O_9Cl:Eu$ by other groups.^{15–17} It should be noted that all previously reported samples were prepared at high temperatures in a reducing atmosphere (N_2/H_2) for the reduction of the Eu^{3+} to Eu^{2+} . Thus, it is noteworthy that

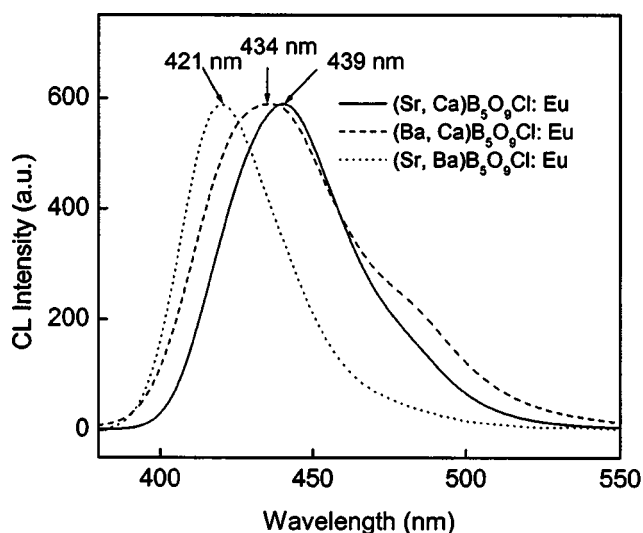


FIG. 2. CL for thin films of binary system of Eu-doped alkaline earth chloroborate deposited at 450 °C and annealed at 800 °C for 2 min in air.

our films of $M_2B_5O_9Cl:Eu$ had blue emission when the films were annealed in air at temperatures suitable for the use of glass substrates. The abnormal reduction of $Eu^{3+} + e \rightarrow Eu^{2+}$ could be related to the rigid three-dimensional network of BO_4 tetrahedra, which is necessary to stabilize the divalent rare-earth ions in an oxidizing atmosphere. In the case of $M_2B_5O_9Cl:Eu$, boron atoms coordinate with three or four oxygen atoms to form BO_3 and BO_4 infrastructures, and these infrastructures comprise the (B_5O_9) network.¹⁶ As a result, a negative M^{2+} vacancy was formed when three M^{2+} ions were replaced by only two Eu^{3+} ions. For this reason, the abnormal reduction was attributed to thermal stimulation of electron transfer from this defect to Eu^{3+} . Usually, the reduction temperature of Eu^{3+} in borates depends on the structure of the boron units. However, the $Ba_2B_5O_9Cl:Eu$ films produced more efficient monochromatic blue CL due to Eu^{2+} after thermal annealing in air compared with $Sr_2B_5O_9Cl:Eu$ films.^{9,10} Consequently, the results shown in Fig. 1 provide further evidence that the cation of $M_2B_5O_9Cl:Eu$ could affect the effectiveness of the reduction process.

Table I illustrates that the dominant and peak wavelength of $M_2B_5O_9Cl:Eu$ shifted over a range of 30 nm as M changed from Ca to Ba . This influence of the ionic radius of the alkaline earth ion on the emission band shift is attributed to a crystal-field effect.^{15,18} 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 $4f^65d$ state to lower energies. Because of this effect, the peak wavelength of the blue emission may be adjusted in the film by combining various alkaline earth ions in the compound. Figure 2 shows the main emission peaks of Eu-doped chloroborate thin films containing alkaline earth pairs deposited at 450 °C and annealed at 800 °C for 2 min in air. The parameters of the three mixed systems are also illustrated in Table I. The peak wavelengths of the three compounds are between the peak wavelengths of $Ba_2B_5O_9Cl$ and $Ca_2B_5O_9Cl$. The peak wavelengths of binary cation films are slightly longer than those calculated on the basis of cation atomic fractions. Additionally, the emis-

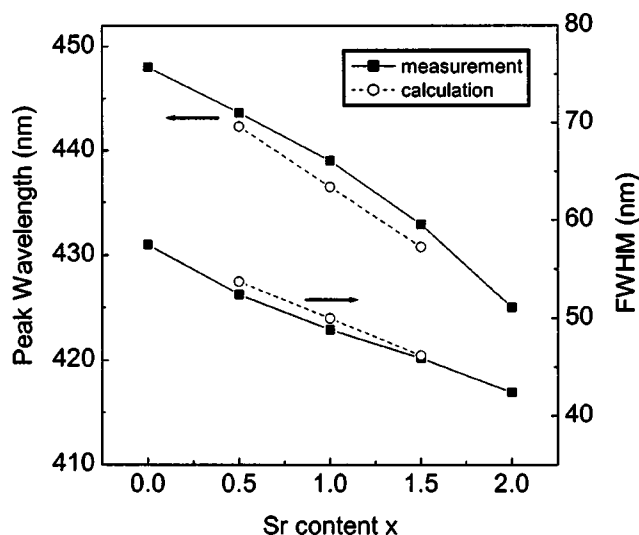


FIG. 3. The dependence of peak wavelength and FWHM on the Sr content x in $(\text{Sr}_x\text{Ca}_{2-x})\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ annealed films.

sion bands of $(\text{Sr},\text{Ba})\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ and $(\text{Sr},\text{Ca})\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ are slightly narrower than calculated values. On the contrary, $(\text{Ba},\text{Ca})\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ had a larger FWHM value compared to the calculated one (60 versus 48 nm), possibly because an unresolved shoulder existed at longer wavelength.

As an illustration, Fig. 3 shows the dependence of the peak wavelength and FWHM on the Sr content in $(\text{Sr}_x\text{Ca}_{2-x})\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ films. All films were deposited at 450 °C, and then annealed in air at 800 °C for 2 min. As expected, both peak wavelength and FWHM decrease when the Sr content increases. However, the measured values for peak wavelength are always larger and FWHM values are always smaller than those calculated on the basis of atomic fraction. The different efficiency of the alkaline earth ions in the mixed systems is probably the reason for the differences between experimental and calculated quantities. The combined effect of crystal-field splitting depends on the type and size of cation complexes. It has been established that with increasing radius of the host lattice cation in an isostructural series of compounds, the relaxation in the $4f^65d$ excited state of Eu^{2+} becomes more restricted.¹⁵ The smaller Stokes shift is also reflected in narrower emission bands with a

smaller FWHM value. In addition, these deviations are likely related to the defects and/or impurity segregation at grain boundaries during the reaction of binary system. Those microstructures will either perturb the crystal field around the Eu^{2+} ion or introduce nonradiative traps in the band gap.¹⁹ More investigation is required to understand the exact mechanism.

In conclusion, thin-film blue phosphors of $\text{M}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ were prepared using spray pyrolysis of an aqueous solution. A change in type and/or composition of alkaline cation in compounds may alter the dominant wavelength from 435 to 465 nm. This observation opens up a possibility of tuning blue emission of other alkaline earth oxide-based hosts by combining other alkaline earth elements, such as Ca and/or Ba. It is noteworthy that these films have been activated in air at temperatures suitable for the use of glass substrates.

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