

Green, blue, and yellow cathodoluminescence of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ thin-films doped with Tb^{3+} , Tm^{3+} , and Mn^{2+}

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Green, blue, and yellow cathodoluminescence (CL) have been obtained for thin-films of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ doped with Tb^{3+} , Tm^{3+} , and Mn^{2+} , respectively. These phosphor films were deposited by spray pyrolysis, and then activated in air at temperatures suitable for use on glass substrates. The CL characteristic peaks of the films correspond to transitions between electronic energy levels of Tm^{3+} , Tb^{3+} , and Mn^{2+} ions. The chromaticity coordinates, dominant wavelength, and color purity were determined for each phosphor. Saturation effects were observed as the beam current density increased. The more severe current saturation of Mn-doped film may be due to a greater ground state depletion of Mn luminescent centers than that of the Tb and Tm. © 2003 American Institute of Physics. [DOI: 10.1063/1.1565704]

Studies of the luminescence of compounds doped with rare-earth elements are required both to determine material properties and to develop practical applications such as flat panel displays and x-ray imaging systems. Compared to powder phosphor layers, thin-film phosphors have such advantages as higher resolution, lower outgassing, etc.¹⁻³

Recently, several groups⁴⁻⁷ have reported the luminescent properties of powders of Sr-based borates such as $\text{SrB}_6\text{O}_{10}$, SrB_4O_7 , and $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ doped with various ions (Eu^{2+} , Sm^{2+} , and Tm^{2+}) and concluded that borates containing the tetrahedral borate group BO_4 were very suitable hosts for various luminescent ions. Less attention has been given to other alkaline earth-based borates. In our recent work,⁸ Eu^{3+} was found to be reduced to Eu^{2+} more efficiently in thin films of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ than in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$, indicating that the cation structures of borates have an influence on the electron transfer. This abnormal reduction of Eu^{3+} ions in $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ could occur at temperatures as low as 140 °C. After either conventional or rapid thermal annealing in air, the films produced efficient highly monochromatic blue cathodoluminescence (CL) due to Eu^{2+} . Thus, the specific crystal structure of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ was effective in reducing Eu^{3+} to its corresponding divalent state Eu^{2+} even without need to introduce reducing agents. Similar to europium ions, other lanthanide ions, such as terbium (Tb) and thulium (Tm), and some transition ions such as manganese (Mn) also have more than one oxidation state. It would be interesting to determine if this effect in $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ occurs for these elements.

In this work, we report the use of spray pyrolysis to grow thin films of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ doped separately with Tm^{3+} , Tb^{3+} , and Mn^{2+} . The CL properties of these films were characterized. In particular, all phosphors here were activated in air at temperatures suitable for glass substrates, which are

used in a number of applications such as field emission displays. In addition, the preparation of thin films by the spray pyrolysis method is attractive for large-scale and large-area production.

Thin films of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ doped with thulium, terbium, and manganese ions were deposited by spray pyrolysis on Corning 7059 glass. The spray pyrolysis method was reported previously.⁹ In brief, stock precursor solutions of BaCl_2 and H_3BO_3 were mixed separately with $\text{Tm}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$, and $\text{Mn}(\text{NO}_3)_2$ in appropriate ratios to provide solutions of various dopant concentrations relative to Ba in $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$. The spray was developed by an ultrasonic nebulizer and was directed towards the substrate by a carrier gas of humid air at a flow rate of 1.2 l/min. The spray chamber was mounted on an $x-y$ translation table to raster the aerosol to cover an area of $2.5 \times 5.0 \text{ cm}^2$. The substrate temperature was 300 °C. 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 CL and luminance measurements were as described earlier.⁸

X-ray diffraction (XRD) spectra in our previous work showed that $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ films were formed by spray pyrolysis at 400 °C.⁸ The as-grown film deposited at 300 °C was amorphous or consisted of very small crystallites. After annealing at 630 °C for 1 h or at 800 °C for 2 min, the film had an XRD that was still consistent with the tetragonal structure of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ with ($a = 11.58$ and $c = 6.69$) and four formula weight units per cell.

Figure 1 shows the CL spectra resulting from 5 kV beam excitation at room temperature for $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ films doped separately with 2% Tm, Tb, and Mn. These films were annealed in air at 630 °C for 1 h. The films that were rapidly annealed at 800 °C had similar CL spectra. It is well known that Tm-activated phosphors have complicated energy level schemes due to the strong deviation from Russell-Saunders coupling in the ($4f$) configuration. As a consequence, the

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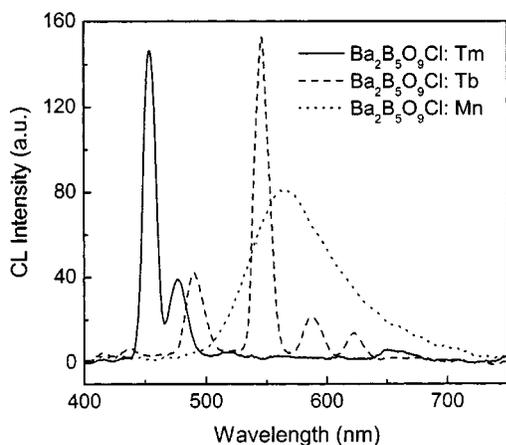


FIG. 1. CL spectra for Tb-, Tm-, and Mn-doped $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ films with a 2% concentration of the dopant in the spray solutions. These films were deposited at 300 °C and annealed in air at 630 °C for 1 h.

relaxation of excited states of Tm^{3+} ions may take place via a large number of relaxation paths and result in UV, visible, and infrared emission.¹⁰ Figure 1 shows that major blue emission peaks of the Tm doped film occurred at 454 and 476 nm, which correspond to the transitions $^1D_2-^3F_4$ and $^1G_4-^3H_6$, respectively. The transition $^1G_4-^3F_4$ is related to the minor emission peak at 650 nm. The CL emission of Tm in $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ films exhibited features similar to those obtained for this ion in other host films,^{11,12} and single crystal.¹³ For Tb^{3+} , Fig. 1 shows peaks that are characteristic of transitions between electronic energy levels of Tb^{3+} ions. The major peak centered at 546 nm corresponds to the transition $^5D_4-^7F_5$, while the transitions $^5D_4-^7F_6$, $^5D_4-^7F_4$, and $^5D_4-^7F_3$ of the Tb ion are related to the emission peaks at 489, 587, and 623 nm, respectively. These emissions are similar to those observed in $\text{Y}_{3-x}\text{Al}_5\text{O}_{12}:\text{Tb}_x^{3+}$ powders.¹⁴ For the Mn-doped sample, a relatively broad yellow emission centered between 565 and 585 nm associated with electronic energy levels of Mn^{2+} ions.

Previous work⁴⁻⁷ showed that Eu^{3+} , Tm^{3+} , and Sm^{3+} could be reduced to the corresponding divalent rare-earth ions in some borates that contain the tetrahedral BO_4 group. The abnormal reduction could even be done in air at high temperature without the introduction of reducing agents. The rigid three-dimensional network of BO_4 tetrahedra is necessary to stabilize the divalent rare-earth ions at high temperature in an oxidizing atmosphere. A model based on the nature of substitution defects was proposed to explain the abnormal reduction.¹⁵ Furthermore, Mn^{2+} and Pb^{2+} were found to retain the divalent state in $\text{SrB}_6\text{O}_{10}$ when fired in air.^{16,17} It is well known that a reduction to the divalent state is not general for all rare-earth dopants. In oxides terbium can occur in the trivalent and tetravalent states but not in the divalent state. On the other hand, reduction of thulium to the divalent state is far more difficult than for europium and has been achieved only in a few borates. Consequently, it is not surprising that the corresponding reduction of Tm^{3+} and Tb^{3+} in $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ was minimal as shown in Fig. 1. For Mn, Fig. 1 shows that the emission was due to the Mn^{2+} even when $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ was annealed in air. Obviously, Mn was not oxidized to any of its higher valences such as +3, +4, and +5. Perhaps the three-dimensional $(\text{B}_5\text{O}_9)_\infty$ network in

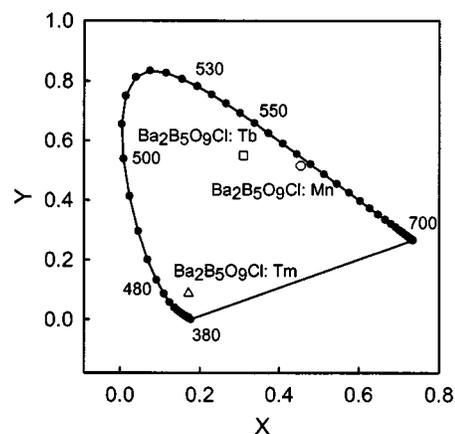


FIG. 2. CIE chromaticity diagram showing the chromaticity points of Tb-, Tm-, and Mn-doped $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ films.

$\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ stabilizes Mn^{2+} even under oxidizing conditions during heat treatment.

The location of the color coordinates of each film on the CIE chromaticity diagram is presented in Fig. 2. Table I lists the chromaticity coordinates, dominant wavelength, and color purity. The results were similar to those obtained for thin films of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$.¹⁸ In comparison with the blue phosphor $\text{Y}_2\text{O}_3:\text{Tm}$ in our previous study,¹² the Tm-doped $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ film had better CIE properties. On the other hand, the coordinates of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}:\text{Tb}$ were not as good as those obtained for the $\text{Y}_2\text{O}_3:\text{Tb}$ film phosphor.

Figure 3 shows the normalized efficiency as a function of beam current density at a constant voltage of 5 kV for the three phosphors. The starting luminance was 59, 20, and 2.3 cd/m^2 at a current density between 5 and 8 $\mu\text{A/cm}^2$ for the Mn-, Tb-, and Tm-doped $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ films, respectively. Accordingly, the efficiency was about 1.91, 0.54, and 0.05 lm/w for the Mn-, Tb-, and Tm-doped samples, respectively. The decrease in efficiency observed as current density increased for all phosphors is related to the saturation effect usually existing in phosphors. Compared to the Tm and Tb doped phosphors, the efficiency of Mn doped $\text{Ba}_2\text{B}_5\text{O}_7\text{Cl}$ film decreased more severely. The physical processes responsible for saturation could be complex, with several mechanisms contributing, including ground state depletion and thermal quenching.¹⁹ The thermal quenching contribution to saturation is due to a heating of the phosphor material during irradiation and, as a consequence, to an increase in the nonradiative decay rate. It has been shown that ground state depletion is directly proportional to the luminescence decay time, and phosphors with shorter decay times are more resistant to current saturation because of activator recycling.^{2,20} The sharper decrease in efficiency observed for the Mn-doped $\text{Ba}_2\text{B}_5\text{O}_7\text{Cl}$ film in Fig. 3 from 5 to 50 $\mu\text{A/cm}^2$ may be due to ground state depletion of Mn luminescent centers

TABLE I. Chromaticity coordinates, dominant wavelength, and purity for green, blue, and yellow phosphor films.

Phosphor films	CIE (x,y)	Dominant wavelength (nm)	Purity (%)
$\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}:\text{Tb}$	(0.310,0.550)	550	61
$\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}:\text{Tm}$	(0.172,0.088)	465	83
$\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}:\text{Mn}$	(0.455,0.514)	575	92

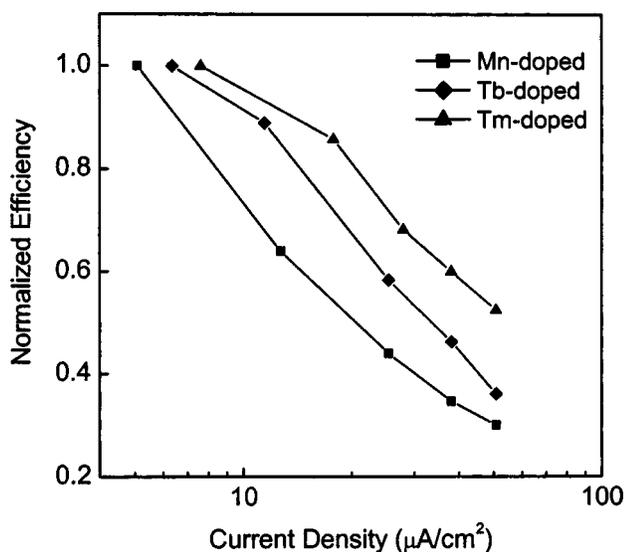


FIG. 3. Normalized efficiency of Tb-, Tm-, and Mn-doped $Ba_2B_5O_9Cl$ films at 5 kV as a function of beam current density.

as a result of longer decay rates because the transition is both spin and parity forbidden. In fact, Mn^{2+} in $ZnGa_2O_4$ was reported to have a long decay constant ranging from 4 to 10 ms.²¹ Analysis of the normalized efficiency data at higher current densities may be considered to the contribution from other mechanisms and phosphor instability. More research work is needed to understand the nature of saturation effects in $Ba_2B_5O_9Cl$ films doped with Tb, Tm, and Mn.

In summary, spray pyrolysis was used to prepare thin films of $Ba_2B_5O_9Cl$ doped with Tb^{3+} , Tm^{3+} , and Mn^{2+} . Unlike Eu in $Ba_2B_5O_9Cl$ host, annealing in air did not reduce the dopants, Tm and Tb. The peaks of the CL spectra at room temperature were characteristic of transitions between

electronic energy levels of Tb^{3+} , Tm^{3+} , and Mn^{2+} ions. The chromaticity coordinates, dominant wavelength and purity for each phosphor were near the values required for field emission displays. Saturation effects were observed at high current density for the three phosphors.

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