

## Cathodoluminescence and Longevity Properties of Potential $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$ (M = Ba or Ca) Green Phosphors for Field Emission Displays

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We report the cathodoluminescence and aging properties of a series of green phosphors of formula  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  ( $x = 0.0-1.0$ , M = Ba or Ca) that have potential applications in field emission displays (FEDs). The series of phosphors was synthesized via NaBr-aided solid-state reactions in a flowing  $\text{H}_2\text{S}$  stream. A low level (~20%) of Ba or Ca substitution for Sr in  $\text{SrGa}_2\text{S}_4:\text{Eu}$  maintains the orthorhombic phase of pure  $\text{SrGa}_2\text{S}_4:\text{Eu}$  phosphors. Further, a low level (~20%) of Ba or Ca substitution for Sr in  $\text{SrGa}_2\text{S}_4:\text{Eu}$  provides various green colors and sufficient brightness for FED applications. Substitution of Ba or Ca for Sr in  $\text{SrGa}_2\text{S}_4:\text{Eu}$  also improved the stability of the phosphor when it was operated under electron-beam irradiation of 5 kV.

**Key Words** :  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  (M = Ba or Ca), Cathodoluminescence, FED

### Introduction

Field emission displays (FEDs) are at the forefront of research into thin flat-panel displays. One of the main priorities of FED research is to find and develop phosphors that exhibit high luminescent efficiency under low- (< 2 kV) and moderate-voltage e-beam excitation (2~10 kV). The principal operating parameters of a FED are the anode operating voltage, the peak current density, and the duty cycle, which all must be taken into account in the selection of a FED phosphor.<sup>1,2</sup> In particular, FEDs have a longer pixel address time (~30  $\mu\text{s}$ ) than cathode ray tubes (CRTs). Stoffer *et al.* suggested that this long dwell time enables the activator recycling of emission light.<sup>2,3</sup> Activator recycling is only possible if the dwell time is longer than the decay time of the activator. It was proposed that thiogallate phosphors activated by either  $\text{Ce}^{3+}$  or  $\text{Eu}^{2+}$  could be used in FEDs, because  $\text{SrGa}_2\text{S}_4:\text{Eu}$  and  $\text{SrGa}_2\text{S}_4:\text{Ce,Na}$  have allowed transitions and a short decay time. Since then, many researchers have studied the cathodoluminescence (CL) properties of, and synthesis methods for, thiogallate phosphors for use in low-voltage (< 2 kV) FEDs.<sup>3-7</sup> These reports indicated that Eu or Ce doped thiogallate phosphors exhibit excellent intrinsic efficiency, color purity, and current saturation behavior. Recent studies have also shown that the luminescence efficiencies of  $\text{SrGa}_2\text{S}_4:\text{Eu}$  and  $\text{CaGa}_2\text{S}_4:\text{Eu}$  are little affected by thermal quenching,<sup>8-10</sup> and have confirmed that  $\text{SrGa}_2\text{S}_4:\text{Eu}$  and  $\text{CaGa}_2\text{S}_4:\text{Eu}$  are suitable phosphors for lighting and display devices, especially for applications where heat effects are expected. However, the operational voltage requirements of FEDs have changed from low voltages (< 2 kV) to moderate voltages (2-10 kV), because carbon nanotube (CNT)-FEDs use higher voltage e-beams than Spindt-type FEDs in order to obtain greater brightness and longer lifetimes.<sup>11</sup> For applied voltages of 2-10 kV, however, there is limited information about the CL proper-

ties of ternary thiogallate green phosphors for use in CNT-FED applications.<sup>12</sup> Moreover, there are few reports on the optical properties of solid solutions of  $\text{SrGa}_2\text{S}_4:\text{Eu}$  and  $\text{M}\text{Ga}_2\text{S}_4:\text{Eu}$  (M = Ba or Ca) phosphors for use in moderate-voltage CNT-FED applications. To determine which quaternary thiogallate green phosphor is most suitable for use in moderate-voltage CNT-FEDs, it is necessary to improve our fundamental understanding of the CL properties of tunable  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  phosphors ( $x = 0.0-1.0$ ; M = Ba or Ca). In particular, determining how the locations of the CL emission peaks and brightness of  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  phosphors vary with changes in both end elements would be very helpful for designing color coordinates. In the present study, we examined the CL and lifetime properties of  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  ( $x = 0.0-1.0$ ; M = Ba or Ca) phosphors, and systematically investigated the influence of composition and crystal structure on the CL, decay, and longevity characteristics of these phosphors and on their Commission International de l'Éclairage (CIE) color coordinates, with the aim of assessing their suitability as green phosphors for use in FEDs.

### Experimental

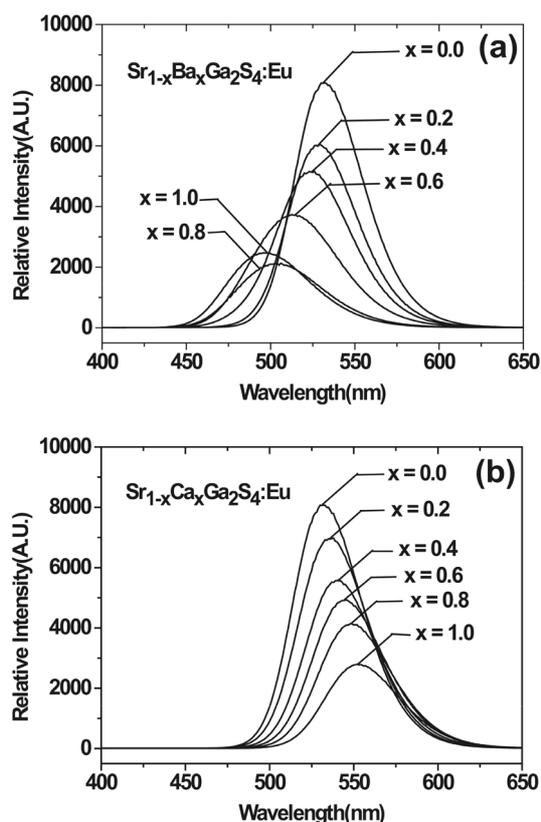
$\text{SrCO}_3$ ,  $\text{MCO}_3$  (M = Ba or Ca), and  $\text{Ga}_2\text{O}_3$  were used as starting materials for the host, and  $\text{Eu}_2\text{O}_3$  was introduced as the activator. Appropriate amounts of NaBr and sulfur were added as a flux to decrease the calcination time and to enhance the luminescence intensity.<sup>13</sup> The starting materials were weighed stoichiometrically, mixed and ground with a mortar and pestle, and then placed in an alumina crucible that was heated in a box-type furnace at 800 °C for 2 h in a flowing  $\text{H}_2\text{S}$  stream. The gas was replaced by Ar to prevent the oxidation of the mixture at temperatures below 500 °C during the initial and final heat-treatment stages. The resulting sintered phosphor cake was removed from the furnace and ground with a mortar and pestle, washed, and

sieved prior to evaluation. X-ray diffraction (XRD) patterns of the  $Sr_{1-x}M_xGa_2S_4:Eu$  powdered phosphors ( $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ ;  $M = Ba$  or  $Ca$ ) were obtained using an X-ray diffractometer (PW1800, Philips) with  $CuK\alpha_1$  radiation. Diffraction patterns were obtained over the range  $10^\circ < 2\theta < 70^\circ$  with a scan rate (for  $2\theta$ ) of  $1^\circ/\text{min}$ . The particle shapes and sizes of the resulting phosphor powders were qualitatively assessed using scanning electron microscopy (SEM; JSM-5300, JEOL).

Photoluminescence (PL) emission was measured using a spectrum analyzer (DARSA II, PSI) with a 27.5 cm monochromator, a photomultiplier (PM) tube, and a 500 W Xe lamp as the excitation source. The incident beam was perpendicular to the surface of each sample, and the observation angle was  $45^\circ$  relative to the excitation source. PL decay measurements were made with a pulsed Nd-YAG laser (Continuum Minilite, 355 nm, 50  $\mu\text{J}$  per pulse, 5 ns pulse length) with a repetition rate of about 10 Hz. The decays were analyzed with a PM (Hamamatsu R928) and an oscilloscope (LeCroy LT 372). CL measurements were carried out in a high-vacuum ( $1 \times 10^{-6}$  Torr) chamber under various excitation energies. Patch-type samples were prepared on metal holders. The phosphor patches were placed in a demountable cathode ray tube and excited with an electron beam with various continuous wave (CW) excitation energies. For the aging study, the cathodoluminescence intensity was measured as a function of time at 5 kV using CW and a peak current density of  $3 \mu\text{A}/\text{cm}^2$ .

### Results and Discussion

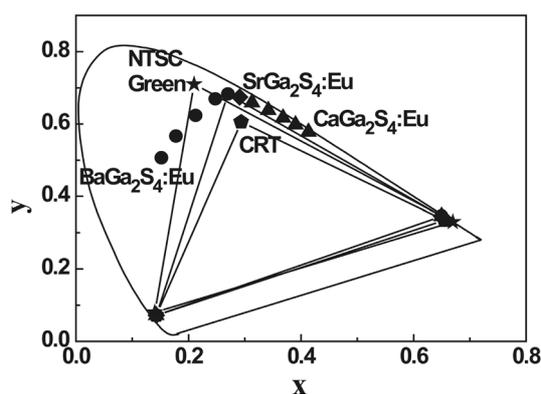
Polycrystalline powders of the  $Sr_{1-x}M_xGa_2S_4:Eu$  phosphors ( $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ ;  $M = Ba$  or  $Ca$ ) were prepared via NaBr-aided high-temperature solid-state reactions, and the XRD patterns of their end members were found to coincide with those reported in the corresponding JCPDS cards and previous publications.<sup>14,15</sup> As previously reported, the XRD pattern of the  $BaGa_2S_4:Eu$  phosphor shows that it is cubic and not isomorphous with the orthorhombic crystal of  $SrGa_2S_4:Eu$ .  $Sr_{0.6}Ba_{0.4}Ga_2S_4:Eu$  powder samples exhibit mixed phases corresponding to the  $BaGa_2S_4$  cubic and  $SrGa_2S_4:Eu$  orthorhombic crystals. Below 20% substitution of Ba for Sr ions in the  $SrGa_2S_4:Eu$  phosphors, the Sr-thiogallate orthorhombic phase is dominant. It was also found that the  $BaGa_2S_4$  cubic phase is dominant above 60% substitution of Ba for Sr ions in  $SrGa_2S_4:Eu$  phosphors. In contrast to the phases of  $Sr_{1-x}Ba_xGa_2S_4:Eu$  phosphors, the XRD patterns of  $SrGa_2S_4:Eu$  and  $CaGa_2S_4:Eu$  are qualitatively similar, and that their structure is the orthorhombic  $PbGa_2Se_4$  phase. The XRD results also indicate that the powder samples of  $Sr_{1-x}Ca_xGa_2S_4:Eu$  phosphors were all single phase with orthorhombic  $PbGa_2Se_4$  structures. Therefore, Ca substitution in  $SrGa_2S_4:Eu$  phosphors results in a trend that is different to that of Ba substitution in  $SrGa_2S_4:Eu$  phosphors. As reported previously,<sup>14,15</sup> the XRD patterns of all the  $Sr_{1-x}M_xGa_2S_4:Eu$  ( $M = Ba$  or  $Ca$ ) phosphors indicate that a low level ( $\sim 20\%$ ) of Ba or Ca substitution for Sr in



**Figure 1.** Cathodoluminescence spectra under electron beam excitation under 5 kV and  $3 \mu\text{A}/\text{cm}^2$  (a)  $Sr_{1-x}Ba_xGa_2S_4:Eu$  and (b)  $Sr_{1-x}Ca_xGa_2S_4:Eu$  phosphors ( $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ ) at room temperature.

$SrGa_2S_4:Eu$  maintains the orthorhombic phase of pure  $SrGa_2S_4:Eu$  phosphors, and they also indicate the absence of residual impurities in these samples.

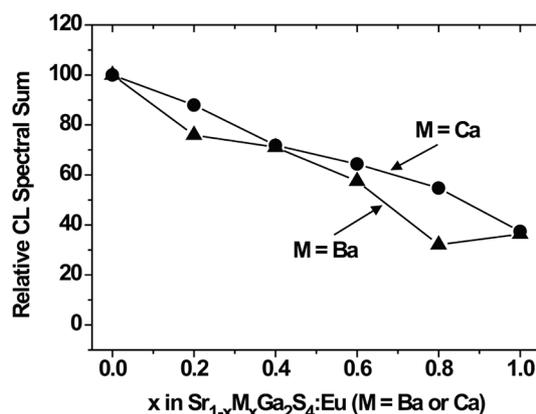
Consistent with previously reported PL emission spectra,<sup>14,16</sup> the CL emission spectra of the  $Sr_{1-x}M_xGa_2S_4:Eu$  phosphors shown in Figure 1 indicate that increasing the Ba composition causes blue-shift behavior in the CL peak: the CL peak of  $SrGa_2S_4:Eu$  is located at 533 nm, whereas that of  $BaGa_2S_4:Eu$  lies at 498 nm, indicating an emission-color tuning range of about 35 nm. The blue-shift behavior can be interpreted in terms of the crystal field strength at the divalent cation site in  $Sr_{1-x}Ba_xGa_2S_4:Eu$ , where the divalent cation is replaced by the  $Eu^{2+}$  ion. The crystal field strength of the  $Eu^{2+}$  ion in the divalent-ion site in  $Sr_{1-x}Ba_xGa_2S_4:Eu$  is proportional to the inverse of the cation-to-anion distance. The crystal field strength decreases with increases in the number of  $Ba^{2+}$  ions in  $Sr_{1-x}Ba_xGa_2S_4$ . Thus the blue-shift of the CL peak originates from the  $4f^{65d^1(a_1)} \rightarrow 4f^7$  transitions of the  $Eu^{2+}$  ions, and follows the previously reported behavior.<sup>13</sup> However, the peak position of the  $Sr_{1-x}Ba_xGa_2S_4:Eu$  phosphors was found to vary unsystematically from the green of  $SrGa_2S_4:Eu$  to the blue-green of  $BaGa_2S_4:Eu$ , which occurs because Ba- and Sr-thiogallates have different structures, and solid solutions in the Ba-Sr systems are limited. In contrast to the  $Sr_{1-x}Ba_xGa_2S_4$  system, the crystal field strength increases with increases in  $Ca^{2+}$  ion numbers in



**Figure 2.** CIE chromaticity coordinates of  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  phosphors ( $\text{M} = \text{Ba}$  or  $\text{Ca}$ ;  $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ ) and the  $\text{ZnS}:\text{Cu,Al}$  green phosphor. Color gamuts of NTSC, a CRT phosphor set, and a FED phosphor ( $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{Ga}_2\text{S}_4:\text{Eu}$  thiogallate green + CRT red and blue) set.

$\text{Sr}_{1-x}\text{Ca}_x\text{Ga}_2\text{S}_4$ . Thus increasing the Ca proportion results in red-shift behavior in the CL peak and in an emission-color tuning range of about 20 nm. The isostructural Ca- and Sr-thiogallates form a complete series of solid solutions with peak positions that vary uniformly from the green of  $\text{SrGa}_2\text{S}_4:\text{Eu}$  to the yellow of  $\text{CaGa}_2\text{S}_4:\text{Eu}$ . As shown in Figure 1, the CL emission bands of  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  ( $\text{M} = \text{Ba}$  or  $\text{Ca}$ ) phosphors are relatively broad and, depending on the host cation, peak in blue-green through yellow regions of the emission spectrum. Therefore, the choice of composition of the  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  ( $\text{M} = \text{Ba}$  or  $\text{Ca}$ ) phosphors results in an emission-color tuning range of about 55 nm.

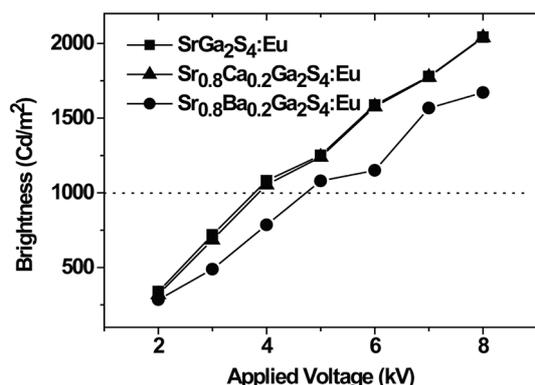
The CIE chromaticity coordinates of the CL spectra of various green-emitting thiogallates are shown in Figure 2. The CIE chromaticity coordinate is a very important property at moderate excitation voltages in full color FED applications because it affects the ratios of the three basic colors. The CIE chromaticity coordinates of  $\text{SrGa}_2\text{S}_4:\text{Eu}$  powders are  $x = 0.27$  and  $y = 0.69$ . The chromaticity coordinates of  $\text{SrGa}_2\text{S}_4:\text{Eu}$  are excellent for a green phosphor and better than those of the commercially available green phosphor used in cathode ray tubes (CRTs) ( $\text{ZnS}:\text{Cu,Al}$ ,  $x = 0.31$  and  $y = 0.60$ ). As the amount of Ba in the  $\text{Sr}_{1-x}\text{Ba}_x\text{Ga}_2\text{S}_4:\text{Eu}$  phosphor is increased, the CIE chromaticity coordinates shift towards those of the greenish blue-emitting  $\text{BaGa}_2\text{S}_4:\text{Eu}$  phosphor ( $x = 0.13$  and  $y = 0.51$ ). Up to 40% substitution of Ba in  $\text{Sr}_{1-x}\text{Ba}_x\text{Ga}_2\text{S}_4:\text{Eu}$  phosphors, the quaternary (Ba,Sr)-thiogallates still exhibit excellent green colors, compared with the  $\text{ZnS}:\text{Cu,Al}$  green phosphor used in CRTs. It is also interesting that even low levels (~20%) of substitution of Ba for Sr actually improve the color slightly. Upon substitution of Ca for Sr in  $\text{SrGa}_2\text{S}_4:\text{Eu}$  phosphors, the CIE chromaticity coordinates converge to those of the pure greenish-yellow-emitting  $\text{CaGa}_2\text{S}_4:\text{Eu}$  phosphors ( $x = 0.41$ ,  $y = 0.58$ ) as the amount of  $\text{CaGa}_2\text{S}_4:\text{Eu}$  phosphor increases. As for Ba substitution, up to 40% substitution the quaternary (Ca, Sr)-thiogallates still exhibit excellent green colors, compared with the green phosphor currently used in CRTs. Figure 2 also shows the color gamut calculated for national television



**Figure 3.** Relative spectral sum of the CL emission spectrum as a function of the Ba or Ca content of the  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  quaternary phosphors.

system committee (NTSC) and measured for the color coordinates of the RGB phosphor set for conventional CRTs and FEDs including quaternary thiogallate green. The color gamut is defined as the area of the triangle within the RGB chromaticity coordinates. When the  $\text{Y}_2\text{O}_3:\text{Eu}$ , and  $\text{ZnS}:\text{AgAl}$  phosphors were chosen as the red and blue phosphors, respectively, and the  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  ( $\text{M} = \text{Ba}$  or  $\text{Ca}$ ) phosphor was chosen as the green phosphor, the color gamut of the new phosphor set ( $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{Ga}_2\text{S}_4:\text{Eu}$  thiogallate, green;  $\text{Y}_2\text{O}_3:\text{Eu}$ , red; and  $\text{ZnS}:\text{AgAl}$ , blue) for moderate-voltage FEDs was increased by ~17% compared to the conventional RGB phosphor set of CRTs. Therefore, low levels (~20%) of substitution of Ba or Ca for Sr in  $\text{SrGa}_2\text{S}_4:\text{Eu}$  phosphors provides excellent green-colored phosphors that are good candidates for FED applications under ~5 kV excitation.

Figure 3 shows the normalized spectral sums of CL emissions as functions of the Sr/Ba and Sr/Ca composition ratios under 5-kV e-beam excitation. The figure shows that the CL efficiency of these phosphors decreases with decreasing Sr concentration. Increasing the Ba or Ca content in  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  ( $\text{M} = \text{Ba}$  or  $\text{Ca}$ ) phosphors within an orthorhombic structure results in a decrease in the spectral sum of the CL emission, which may be attributable to a complicated effect of substitution on the CL mechanism. When phosphors are excited by an electron beam subject to a moderate voltage (~5 kV), the CL efficiency depends on the combined effects of the following processes: penetration depth of excited electrons, electron-hole pair production, energy transfer to activators, and light emission. However, it is difficult to determine the individual contributions of these distinct effects to the change in the CL efficiency during Ba or Ca substitution. As for crystallography data reported previously,<sup>14</sup> the cell parameters of  $\text{SrGa}_2\text{S}_4$  ( $a = 20.840$ ,  $b = 20.495$ , and  $c = 12.212$ ) are very close to those of  $\text{EuGa}_2\text{S}_4$  ( $a = 20.716$ ,  $b = 20.404$ , and  $c = 12.200$ ). Substituting  $\text{Ba}^{2+}$  (a larger ion) or  $\text{Ca}^{2+}$  (a smaller ion) for  $\text{Sr}^{2+}$  in  $\text{SrGa}_2\text{S}_4:\text{Eu}$  phosphors could change the cell parameters of  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$  ( $\text{M} = \text{Ba}$  or  $\text{Ca}$ ) phosphors relative to those of  $\text{EuGa}_2\text{S}_4$ , and thereby change the crystallographic environment of  $\text{Eu}^{2+}$  ions in  $\text{Sr}_{1-x}\text{M}_x\text{Ga}_2\text{S}_4:\text{Eu}$ . It is speculated that this small

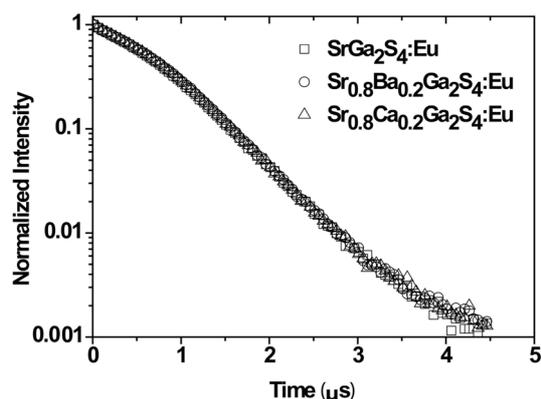


**Figure 4.** Plot of the dependence on applied voltage of the CL brightness of  $SrGa_2S_4:Eu$ ,  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$ , and  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$  phosphors operated under CW excitation with a current density of  $3 \mu A/cm^2$ .

change of the  $Eu^{2+}$  surroundings could reduce the CL efficiency for low levels ( $\sim 20\%$ ) of substitution of Ba or Ca for Sr in  $SrGa_2S_4:Eu$  phosphors.

Although Ba and Ca substitutions into Sr sites in  $SrGa_2S_4:Eu$  phosphors decrease the brightness of Sr-thiogallate, the green color tunability could be used to cover the reduced brightness. We selected samples of  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$  and  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$  in order to determine their suitability for use as green phosphors in FEDs operated under moderate voltages ( $\sim 5$  kV). Figure 4 shows the cathodoluminescence (CL) brightness-operating voltage characteristics of  $SrGa_2S_4:Eu$ ,  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$ , and  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$  phosphors operated under CW excitation with a current density of  $3 \mu A/cm^2$ , measured in reflection mode. It has been estimated in previous publications that green luminescence of  $1000 Cd/m^2$  is required in order to achieve the  $200 Cd/m^2$  of peak white required by a typical display.<sup>17</sup> As shown in Figure 4, only 4 kV is needed for the  $SrGa_2S_4:Eu$  and  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$  phosphors to produce the required luminance. It also shows that 5 kV is required for the  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$  phosphor to produce the brightness required for FEDs. If CNT-type FEDs are operated under more than 5 kV, a low level ( $\sim 20\%$ ) of substitution of Ba or Ca for Sr in  $SrGa_2S_4:Eu$  results in quaternary thiogallates that result in green phosphors in CNT-type FEDs of sufficient brightness.

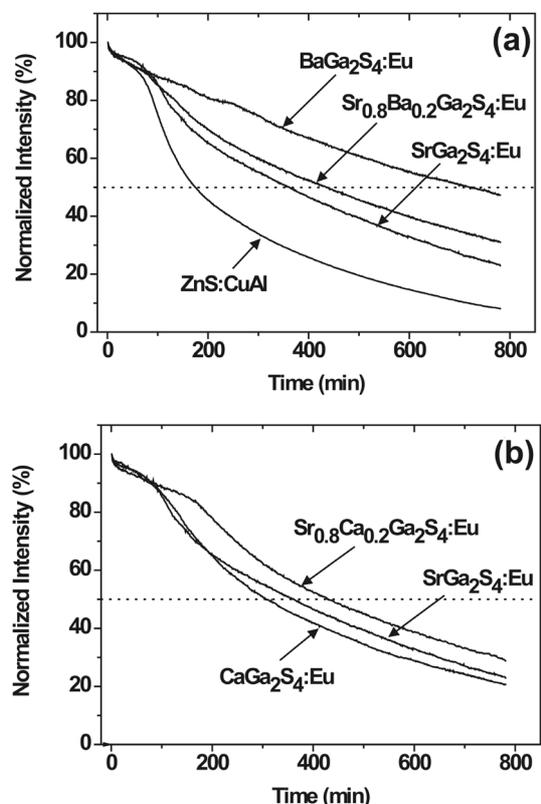
The decay time and saturation effect at a high current density are also important properties of FEDs. In particular, the pixel-addressing time is  $30 \mu s$  in a FED, compared with 10 ns in a CRT. Stoffers *et al.* suggest that the long dwell time of 30 ms leads to activator recycling,<sup>1-4</sup> whereby fast activators can be excited to reemit light many times during this dwell time. Activator recycling would only be possible if the dwell time is longer than the activator decay time. They reported that an  $SrGa_2S_4:Eu$  phosphor containing  $Eu^{2+}$  activators with a short luminescent decay time and at high concentrations produce the desired reduced saturation. Figure 5 shows the fast decay curve of  $SrGa_2S_4:Eu$  ( $1.55 \mu s$ ),  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$  ( $1.57 \mu s$ ), and  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$  ( $1.58 \mu s$ ) phosphors (with 2% Eu) obtained at 300 K. The figure indicates that the decay times (10% decay) for low



**Figure 5.** PL decay curves for the emission at maximum PL wavelengths of  $SrGa_2S_4:Eu$ ,  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$ , and  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$  (2.0%) phosphors under excitation at 355 nm.

levels ( $\sim 20\%$ ) of substitution of Ba or Ca for Sr in  $SrGa_2S_4:Eu$  phosphors are very close to that of pure  $SrGa_2S_4:Eu$  phosphor. Therefore, the fast decay time of these quaternary thiogallates indicates that they can overcome saturation effects.

The aging behavior of  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$ , and  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$  phosphors was also compared to that of  $MGa_2S_4:Eu$  ( $M = Ba, Sr, \text{ or } Ca$ ) and  $ZnS:Cu,Al$  under 5 kV electron excitation with an average current density of  $3 \mu A/cm^2$  after



**Figure 6.** Plots of the CL longevity characteristics of (a)  $SrGa_2S_4:Eu$ ,  $Sr_{0.8}Ba_{0.2}Ga_2S_4:Eu$ ,  $BaGa_2S_4:Eu$ , and  $ZnS:Cu,Al$  phosphors and (b)  $SrGa_2S_4:Eu$ ,  $Sr_{0.8}Ca_{0.2}Ga_2S_4:Eu$ , and  $CaGa_2S_4:Eu$  phosphors, operated under 5 kV CW excitation with a current density of  $3 \mu A/cm^2$ .

780 min excitation. The total electron dose for these curves corresponds to 0.14 C/cm<sup>2</sup>. Consistent with previous reports,<sup>4</sup> SrGa<sub>2</sub>S<sub>4</sub>:Eu exhibits better aging characteristics than ZnS:Cu,Al. As shown in Figure 6(a), the CL luminance of SrGa<sub>2</sub>S<sub>4</sub>:Eu decreases moderately to 23% of its initial value after 780 min excitation, and the CL intensity of ZnS:Cu,Al decreases rapidly to 8% of its initial value after 780 min. For the Sr<sub>0.8</sub>Ba<sub>0.2</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu phosphor, the CL luminance decreases moderately to 31% of its initial value after 780 min excitation. It is apparent that 20% substitution of Ba for Sr in SrGa<sub>2</sub>S<sub>4</sub>:Eu reduces the aging rate, resulting in a final CL intensity of the Sr<sub>0.8</sub>Ba<sub>0.2</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu phosphor that is more than 1.3 times that of the SrGa<sub>2</sub>S<sub>4</sub>:Eu sample. The final CL intensity of the Sr<sub>0.8</sub>Ba<sub>0.2</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu phosphor is more than 3.8 times that of the commercialized green ZnS:Cu,Al sample. The enhanced aging properties of the Sr<sub>0.8</sub>Ba<sub>0.2</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu phosphor are due to the reduction in the hydrolysis reaction of BaGa<sub>2</sub>S<sub>4</sub>:Eu induced by the electron beam.<sup>14</sup> Figure 6(b) compares the normalized CL intensities as a function of time under 5 kV electron excitation with an average current density of 3 μA/cm<sup>2</sup> for the SrGa<sub>2</sub>S<sub>4</sub>:Eu, Sr<sub>0.8</sub>Ca<sub>0.2</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu, and CaGa<sub>2</sub>S<sub>4</sub>:Eu phosphors. It clearly shows that the CL luminances of CaGa<sub>2</sub>S<sub>4</sub>:Eu and Sr<sub>0.8</sub>Ca<sub>0.2</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu decrease moderately to 21 and 29% respectively of their initial values after 780 min excitation. Although the pure CaGa<sub>2</sub>S<sub>4</sub>:Eu phosphor has a slightly faster aging rate than pure SrGa<sub>2</sub>S<sub>4</sub>:Eu, Figure 6(b) shows that the final CL intensity of the Sr<sub>0.8</sub>Ca<sub>0.2</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu phosphor is more than 1.25 times that of the SrGa<sub>2</sub>S<sub>4</sub>:Eu sample. It is not clear why a low level of substitution of Ca for Sr in SrGa<sub>2</sub>S<sub>4</sub>:Eu results in enhanced aging properties. However, it is apparent that a low level (~20%) of substitution of Ba or Ca for Sr provides enhanced CL aging curves for SrGa<sub>2</sub>S<sub>4</sub>:Eu phosphors, confirming that one of these quaternary thiogallates exhibits good longevity when used as a green phosphor in CNT-type FEDs.

### Conclusion

Green Sr<sub>1-x</sub>M<sub>x</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu ( $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ , M = Ba or Ca) phosphors were synthesized *via* NaBr-aided solid-state reactions with a H<sub>2</sub>S stream. A low level (~20%) of Ba or Ca substitution for Sr in SrGa<sub>2</sub>S<sub>4</sub>:Eu maintains the orthorhombic phase of pure SrGa<sub>2</sub>S<sub>4</sub>:Eu phosphors. Further, a low level (~20%) of Ba or Ca substitution for Sr in SrGa<sub>2</sub>S<sub>4</sub>:Eu provides various green colors, a fast decay time, and sufficient brightness for CNT-FED applications. Sub-

stitution of Ba or Ca for Sr in SrGa<sub>2</sub>S<sub>4</sub>:Eu also improved the stability of the phosphor when it was operated under electron beam irradiation of 5 kV. The color variations, CL brightness and enhanced longevity properties of these highly efficient Sr<sub>1-x</sub>M<sub>x</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu ( $x = 0.0-0.2$ , M = Ba or Ca) phosphors suggest that they are good candidates for use as green phosphors in FED applications. The CIE color coordinates, brightness and longevity of thiogallate green phosphors can be adjusted for various requirements by selecting the cations in Sr<sub>1-x</sub>M<sub>x</sub>Ga<sub>2</sub>S<sub>4</sub>:Eu ( $x = 0.0-0.2$ , M = Ba or Ca) phosphors.

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