The Formation of Eu$^{2+}$ Clusters in Saturated Red Ca$_{0.5}$Sr$_{0.5}$S:Eu Electroluminescent Devices

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A high-luminance and high-color-purity inorganic phosphor Ca$_{0.5}$Sr$_{0.5}$S:Eu has been developed for the red component in ac thin-film electroluminescent devices using electron-beam evaporation. The influence of the Eu concentration on the luminescence and response characteristic of the Ca$_{0.5}$Sr$_{0.5}$S:Eu devices was studied. A high Eu concentration causes not only concentration quenching of photoluminescence and electroluminescence (EL) emission, but also increases the light-emitting response time of the Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices upon the application of an electric field. Decay characteristics of the Ca$_{0.5}$Sr$_{0.5}$S:Eu thin films point out the creation of nonradiative decay channels due to the formation of Eu$^{2+}$ clusters at high Eu concentrations. The slow light-emitting response in Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices was attributed to the presence of traps generated by these Eu$^{2+}$ clusters. To understand the nature of these traps, the frequency and temperature dependence of the response time was studied.


In the past few years, inorganic thin-film electroluminescent (EL) devices have been actively investigated for applications in full-color flat panel displays. An EL display, with its excellent video performance characteristics, wide viewing angle and wide operating temperature range, simple and rugged structure, and low manufacturing cost has the potential to become an affordable high-definition flat panel display technology.

At present, ZnS:Mn is used as a red component in EL displays. However, to obtain a pure red color, filtering of the ZnS:Mn emission is necessary. This not only complicates the production process of the EL displays but also lowers the emission intensity. Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices exhibit a pure red emission having a peak wavelength of 640 nm and CIE coordinates of (0.67; 0.33), close to the required CIE coordinates for the red component of a modern display (0.65; 0.33) (SMPT-C standard, the Society of Motion Picture and Television Engineers). Filtering is not needed due to its pure red emission, which makes Ca$_{0.5}$Sr$_{0.5}$S:Eu an interesting phosphor.

In our earlier work, a wet chemical synthesis method for Ca$_{0.5}$Sr$_{0.5}$S:Eu powder was developed. Using this powder as a starting material for thin-film deposition was found to enhance the luminescence performance of Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices. The red emission of Ca$_{0.5}$Sr$_{0.5}$S:Eu powder, thin films, and EL devices originates from excitation of the Eu activators. Electrons are excited from the 4f$^7$ ground state of the Eu$^{3+}$ ions to the 4f$^6$ 5d excited state. The emission of Eu-doped phosphors is strongly dependent on the host material. With increasing crystal field the Eu emission color shifts from saturated blue (BaAl$_2$S$_4$:Eu) toward deep red (CaS:Eu). In Ca$_{0.5}$Sr$_{0.5}$S:Eu the 4f$^6$ 5d excited state of the Eu$^{2+}$ activator is situated near the conduction band minimum. Impact-excited Eu$^{2+}$ activators can therefore easily be ionized, which complicates the excitation and emission processes in these EL devices.

To improve the performance of the Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices, an evaluation of the Eu concentration was made. Decay measurements of the photo luminescence (PL) emission of Ca$_{0.5}$Sr$_{0.5}$S:Eu thin films clarify the concentration quenching behavior. The relation between the light-emitting response time of the EL devices upon the application of the electric field and the Eu concentration was thoroughly studied.

Experimental

Ca$_{0.5}$Sr$_{0.5}$S:Eu powder was prepared with a wet chemical synthesis$^1$ starting from an aqueous solution of Ca(NO$_3$)$_2$·4H$_2$O, Sr(NO$_3$)$_2$, and (NH$_4$)$_2$SO$_4$, with the molar ratio of Ca to Sr equal to 0.5:0.5. The sulfate was added in slight excess. The appropriate amount of Eu was added as an aqueous solution of EuCl$_3$ (0.002 M) to reduce concentration errors. The reaction product was dried at 150°C under atmospheric conditions. This powder was then pulverized and pressed into pellets to stimulate the atomic diffusion during the second drying step, this time under a N$_2$ flow at a temperature of 600°C. The resulting powder consists almost entirely of CaSO$_4$ and SrSO$_4$, although the diffraction peaks of the latter one are shifted to slightly higher diffraction angles, indicating a partial substitution of Sr by Ca. In this stage of the production process, no completely homogeneous mixture of Ca and Sr is present. This material is again pulverized, pressed into pellets, and sulfurized under H$_2$S at 1150°C.

To evaluate the influence of the production parameters on the EL characteristics of Ca$_{0.5}$Sr$_{0.5}$S:Eu thin films, double-insulating ac thin-film electroluminescent (ACTFEL) structures were grown by electron-beam evaporation in a Leybold Univex 450 vacuum system (base pressure below 10$^{-3}$ Pa). Thin films were deposited on ITO-coated Corning 1737 substrates. 300-nm Al$_2$O$_3$ (Balzers) thin films were used as insulators. A 600-nm Ca$_{0.5}$Sr$_{0.5}$S:Eu phosphor layer was evaporated at a rate of 2.0 nm/s. During the deposition of this phosphor layer the substrate temperature was 600°C. To reduce the sulfur deficiency of the film, the evaporation took place under a H$_2$S partial pressure of $8 \times 10^{-3}$ Pa, as this gave the best luminescence result.

On both sides of the phosphor layer a 200-nm ZnS buffer layer was incorporated. The influence of ZnS buffer layers is twofold.$^4$ Through a crystalline buffer layer the electrons are accelerated and injected with a higher energy into the phosphor layer. Subsequently there are more “hot” electrons for impact excitation. Furthermore, a ZnS buffer layer on both sides of the phosphor layer prevents diffusion (europium, oxygen) between the insulator and the phosphor layer.

Photoluminescence emission and excitation spectra were recorded with a FS920 luminescence spectrometer (Edinburgh Instruments). Electroluminescent emission spectra and time-resolved measurements were obtained with an intensified charge-coupled device (CCD) (Andor Instruments) attached to a 0.5-m Ebert monochromator.

Results and Discussion

PL and EL emission intensity.— A study of the luminescent and structural characteristics of the Ca$_{0.5}$Sr$_{0.5}$S:Eu powders, thin films, and EL devices as a function of the Eu concentration was performed. Figure 1 shows the absolute PL emission intensity of the
Eu2+ ions in the phosphor layer available for excitation, which results in a higher emission intensity. Nevertheless, at high Eu concentrations another mechanism should be taken into account, namely, concentration quenching.

The concentration quenching also confines the Eu concentration in Ca0.5Sr0.5S:Eu EL devices, meaning that beyond a certain Eu concentration a further increase does not result in a higher lumiance. The highest luminance L40 at 40 V above threshold is obtained for Ca0.5Sr0.5S:Eu EL devices doped with 0.1 mol % Eu (Fig. 1). The different slope of the powder curve compared to that of the thin-film electroluminescent (TFEL) curve could be due to a lower Eu concentration in the thin film evaporated out of the Ca0.5Sr0.5S:Eu powder. The effective Eu concentration in the Ca0.5Sr0.5S:Eu powders and thin films could not be verified. The concentrations given in Fig. 1 are the ones in the starting materials.

To understand this concentration-quenching behavior, PL decay measurements of Ca0.5Sr0.5S:Eu thin films with the Eu concentration as a parameter were performed (Fig. 2). The thin films were excited at 405 nm, obtained with a dye laser. The excitation has a pulse length of about 1 ns and a 2-Hz pulse frequency. The change of the emission intensity of the thin films was measured with the intensified CCD after excitation with the laser pulse.

As seen in Fig. 2, the decay of the PL emission intensity of Ca0.5Sr0.5S:Eu thin films is faster when the Eu concentration increases. The decay profile consists of multiple components. These measurements indicate that at high Eu concentration, Eu2+ ions can form clusters in the phosphor layer. In these Eu2+ clusters energy transfer between the different Eu activators is possible. Electrons captured in these clusters can move from one Eu activator to another. This increases the chance the electrons are trapped at killer centers, such as impurities and lattice defects, where their energy is dissipated nonradiatively. In this way Eu2+ clusters create nonradiative decay channels, resulting in a faster decay of the PL emission intensity.

The creation of nonradiative decay channels, resulting from a high Eu concentration, explains the concentration quenching of both the PL emission of the Ca0.5Sr0.5S:Eu powders and the lumiance of the EL devices (Fig. 1).

Response characteristics of EL devices.— The concentration of Eu in the phosphor layer also has an influence on the light-emitting response time of the EL device upon the application of an electric field. The response time is defined as the time necessary to reach 90% of the maximum emission intensity upon application of the electric field. To measure the response time the waveform shown in Fig. 3 is applied. For a period of 10 ms a waveform with a frequency of 1 kHz is applied. During the following 240 ms the voltage is turned off. The first 10 ms is divided into periods of 250 μs in which the absolute EL emission is measured at 30 V above threshold voltage.

At a Eu concentration of 0.1 mol % the response time measured in this way was 3 ms (Fig. 4). At Eu concentrations higher than 0.6 mol % the response time was more than 5 ms. As expected, a lower Eu concentration results in a faster light-emitting response of the Ca0.5Sr0.5S:Eu EL device when an electric field is applied (Fig. 4).

In previous publications the response characteristics of Eu-doped CaS EL devices were related to the presence of shallow traps in the phosphor layer. To understand the nature of these traps, the frequency and temperature dependence of the response time were studied. The response time of Ca0.5Sr0.5S:Eu EL devices was measured at 70 K and compared to the measurements performed at room temperature (298 K). As seen in Table I, at lower temperature the response time of the EL devices decreases. The influence of temperature on the response time is the largest for EL devices with the highest Eu concentration.

When an electric field is applied to a Ca0.5Sr0.5S:Eu EL device, electrons are excited into the conduction band by field-induced ion-
ization, leaving ionized Eu$^{2+}$ activators. The electrons in the conduction band are transported toward the anode. There they are preferentially captured at the traps generated by the Eu$^{2+}$ clusters, because of their high concentration, before they are captured at the phosphor/insulator interface.

However, in the Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices these traps are energetically located close to the conduction band minimum, which explains the temperature dependence of the response time (Table I). At lower temperature thermal ionization of the trapped electrons to the conduction band is limited. This implies that when the voltage is turned off, the electrons in the shallow traps and the ionized Eu$^{2+}$ centers increase the internal polarization field caused by the electrons at the phosphor/insulator interface. When the electric field is reversed, this internal polarization field is added to the applied field, producing a higher electric field. This stimulates tunnel injection of electrons from the cathodic interface, which enhances the response characteristics of the EL devices (Table I).

At room temperature the electrons at these shallow traps are easily thermally excited to the conduction band when the voltage is turned off. Due to the polarization field generated by the electrons captured at the phosphor/insulator interface, these electrons diffuse back and neutralize the positive space charge created by the ionized Eu$^{2+}$ activators. When the reverse voltage is applied, the positive influence of the internal polarization field on the electric field is restricted, resulting in a slower light-emitting response of the EL devices (Table I). After some time all the shallow traps are filled and the maximum emission intensity is obtained.

Now we can explain why the light-emitting response time increases with the increase in Eu concentration, as seen in Fig. 4. The shallow traps, responsible for the slow light-emitting response of the Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices, are generated by Eu$^{2+}$ clusters. As seen in the previous paragraph, a higher Eu concentration in the phosphor causes concentration quenching of the PL as well as the EL emission intensity due to the formation of Eu$^{2+}$ clusters, which generate the shallow traps. To reach the maximum emission intensity, all the shallow traps have to be filled, which clarifies the increasing response time of the EL device at higher Eu concentrations.

To have a closer look at the decay rate of the shallow traps in the phosphor layer, the waveform in Fig. 3 was adjusted. In a similar way the light-emitting response time of the Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices upon the application of the electric field is measured; however, the period during which the voltage is turned off is decreased from 250 to 90 ms, 40 ms, 10 ms, and finally 2.5 ms. Figure 5 shows the response time of the Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices as a function of the period during which the voltage is turned off and as a function of the Eu concentration in the phosphor layer.

In Fig. 5 the response time is a measurement of the number of shallow traps that are emptied after a certain time. After a turn-off time of 240 ms, most of the shallow traps in the phosphor layer are apparently emptied and we measure the actual light-emitting response time of the EL devices. When the voltage was turned off for only 2.5 ms in the EL devices with 0.1 mol % Eu, still all the traps are filled and the maximum emission intensity is immediately obtained. At higher Eu concentration there are more shallow traps present in the phosphor layer. Subsequently, the number of electrons that are thermally excited to the conduction band is higher. So in these EL devices it will take a certain time to fill all the traps again and reach the maximum emission intensity. The response time of the EL devices with 1.0 and 0.6 mol % Eu increases rapidly when the turn-off time of the voltage rises.

### Conclusions

A highly luminescent and purely red-emitting EL phosphor, Ca$_{0.5}$Sr$_{0.5}$S:Eu, was developed for the red component in EL displays. The highest luminance $L_{40}$ at 40 V above threshold is obtained for Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices doped with 0.1 mol % Eu. At this Eu concentration the EL emission intensity is not quenched, as the formation of Eu$^{2+}$ clusters, through which non radiative decay is made possible, is limited. These Eu$^{2+}$ clusters were also responsible for a slow light-emitting response time of the Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices.

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**Table I.** Response time of Ca$_{0.5}$Sr$_{0.5}$S:Eu EL devices with different Eu concentration at room temperature (298 K) and at 70 K.

<table>
<thead>
<tr>
<th>Eu concentration</th>
<th>Temperature</th>
<th>Response time (ms)</th>
</tr>
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<tbody>
<tr>
<td>0.1 mol % Eu</td>
<td>70 K</td>
<td>2.0 ms</td>
</tr>
<tr>
<td>1.0 mol % Eu</td>
<td>70 K</td>
<td>3.0 ms</td>
</tr>
<tr>
<td></td>
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<td>3.0 ms</td>
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<td></td>
<td>298 K</td>
<td>6.5 ms</td>
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