 Persistent luminescence refers to the type of luminescence which remains for a long time (typically several hours) after removal of the excitation light. Persistent phosphors allow a wide range of applications, such as safety illumination and traffic signs. In the field of (safety) signage, a major advantage is the strongly reduced energy consumption, as the excitation of the phosphors is ideally performed by ambient or day light. Currently, europium-based materials are among the most efficient and most studied materials. Other rare-earth ions are often added to enhance the persistence lifetime. It appears that dysprosium and neodymium are often appropriate for this purpose. Although this type of storage phosphor has attracted a lot of attention in the past decade, much debate is still going on about the exact mechanism of the persistent luminescence. Most authors agree on the trapping of charge carriers (electrons in most cases) on defects, which are then thermally released. The enhancement of the persistent luminescence due to the addition of other rare earths has been related to the position of the codopant’s energy levels, the ionization potential of the codopant, and the creation of additional defects.

An overview of the recently investigated persistent phosphor materials can be found in Ref. 3. The most efficient materials are currently based on SrAl2O4:Eu, Dy3 and Sr2MgSiO4:Eu, Dy emitting in the green and the blue part of the visible spectrum, respectively. Only a relatively small number of red-emitting phosphors have been described in literature, including Ca2SiS4:Eu2+, Ca2SiS4:Eu,Nd. The two emission bands originate from Eu3+ transitions in the green and the blue part of the visible spectrum, respectively. Most authors agree on the trapping of charge carriers (electrons in most cases) on defects, which are then thermally released. The enhancement of the persistent luminescence due to the addition of other rare earths has been related to the position of the codopant’s energy levels, the ionization potential of the codopant, and the creation of additional defects.

We studied the persistent luminescence in europium-doped calcium thiosilicate upon codoping with the rare-earth elements neodymium, dysprosium, samarium, and thulium. The strongest afterglow was observed for neodymium codoping. The persistence emission spectrum is dominated by a band at 660 nm, which makes the afterglow color redshifted compared to the steady-state luminescence. Thermoluminescence measurements revealed different glow curves for the two europium lattice sites in the Ca2SiS4 host, suggesting that transfer of charge carriers via the conduction band is of minor importance. Finally, we conclude that the Nd3+ ions occupy lattice sites in close proximity of the Eu2+ ions, based on site-selective luminescence measurements on Ca2SiS4:Eu,Nd.

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Results and Discussion

Figure 1 shows the persistence decay curves measured at 660 nm for Ca2SiS4:Eu without codopants and with Dy, Nd, Sm, and Tm as codopants. All powders were excited at a wavelength of 320 nm for 5 min. Ca2SiS4:Eu without rare-earth codoping only shows a weak persistent luminescence, and codoping with neodymium or dysprosium is required to obtain considerable persistent luminescence.

The emission in Ca2SiS4:Eu consists of two emission bands, with maxima at 565 and 660 nm. These two emission bands originate from Eu ions substituted on the two different Ca lattice sites.
The ratio between these bands is governed by the europium concentration; the red emission band becomes relatively stronger upon increasing europium concentration. Hence, the emission color can be tuned from yellow to red upon increasing Eu substitution from 0.1 to 2%. For Ca$_2$SiS$_4$:Eu,Nd, the steady-state luminescence is compared to the persistence emission spectrum in Fig. 2.

Clearly, the emission band at 660 nm is relatively stronger than the one at 565 nm during the afterglow, which makes the persistent emission appear considerably redder than the steady-state luminescence. During the persistence decay, the shape of the emission spectrum remains more or less unchanged.

In previous work, we described that the two emission bands in Ca$_2$SiS$_4$:Eu are related to two different sites in the Ca$_2$SiS$_4$ lattice. We also showed that energy transfer from the yellow emission band (peaking at 565 nm) to the red emission band (peaking at 660 nm) occurs, but that the ratio between the bands is independent of the excitation intensity except for high intensities. Consequently, the spectral difference between persistence and steady-state luminescence is of a different origin than merely the difference in intensity of the emitted light.

Figure 3 shows the excitation spectrum for the steady-state PL of the red emission band in Ca$_2$SiS$_4$:Eu,Nd measured at room temperature. The broad excitation band ranging from 360 to 550 nm is composed of two components. The lower-energy side results from the direct excitation of the 4f$^7$ ground state to the lowest 4f$^6$5d excited state of Eu$^{2+}$ on the site related to the red-emitting center, while the higher-energy side is related to the yellow-emitting Eu$^{2+}$ center and subsequent energy transfer. Excitation between 250 and 350 nm is less efficient and related to excitation to higher 4f$^6$5d states. Figure 3 also shows the excitation spectrum of the persistent luminescence, which was measured as described in the Experimental section.

The excitation of the persistent luminescence is strongly different from the steady-state excitation spectrum. Exposing Ca$_2$SiS$_4$:Eu,Dy or Ca$_2$SiS$_4$:Eu,Nd to light in the range from 360 to 500 nm hardly results in any persistent luminescence. For persistent luminescence to occur, excitation in the range from 250 to 350 nm is required, coinciding with the high-energy part of the steady-state excitation spectrum (Fig. 3). Consequently, Ca$_2$SiS$_4$:Eu-based persistent phosphors seem less attractive from a technological point of view, due to the impossibility to excite with visible or near-UV light.

Figure 4 shows the TL glow curve (heating rate of 5 K/min) for both emission centers in Ca$_2$SiS$_4$:Eu and Ca$_2$SiS$_4$:Eu,Nd. Prior to the measurement, powders were cooled to 25 K and excited at 320 nm for 5 min. The shape of the glow curves is determined by the thermal release of trapped carriers (at multiple depths) and the subsequent emission of visible light. One observes in Fig. 4 that the TL emission drops at a temperature of about 400 K. This is not due to the thermal quenching of the emission but to the fact that all traps are then emptied. Indeed, it was verified that the steady-state PL intensity still reached 90% of the room-temperature value at a temperature of 420 K. The quenching temperature (defined as the temperature for which the integrated emission intensity dropped to 50%) was determined at 460 K. Hence, the glow curves presented in Fig. 4 are not significantly altered by the thermal quenching profile.

The glow curve for Ca$_2$SiS$_4$:Eu is almost entirely situated below room temperature, with a mean peak at 230 K as well as some other minor contributions. This explains the weak persistent emission for Ca$_2$SiS$_4$:Eu at room temperature (Fig. 1). From Fig. 4, one observes a difference in TL behavior for the yellow and the red emission band, as the glow curve of the former is shifted by about 30 K to higher temperatures.
Upon codoping with Nd$^{3+}$, several additional contributions on the high-temperature side emerge in the glow curve, for both the yellow and the red emission band, which are responsible for the occurrence of the persistence emission at room temperature. Again, the glow curves are different for both emission centers. As in the persistent luminescence spectrum, the TL spectrum is redder compared to the steady-state PL due to the relatively stronger red emission band.

**Site-selective spectroscopy in Ca$_2$SiS$_4$:Eu,Nd.**—Codoping of Ca$_2$SiS$_4$:Eu with Nd not only enhances the persistent luminescence, but it also adds infrared emission lines to the luminescence spectrum, originating from 4f-4f transitions within Nd$^{3+}$. Transitions from the $^2$F$_{5/2}$ excited state to the $^4$I$_{9/2}$, $^4$I$_{15/2}$, and $^4$I$_{13/2}$ states lead to emission around 0.90, 1.07, and 1.36 μm, respectively (not shown). Due to the shielding effect of the outer s and p electron shells, the 4f-4f transition energies are only slightly affected by the incorporation in the host material. However, the splitting and the center of gravity of the multiplet states depend on the local surrounding of the Nd$^{3+}$ ion. Hence, site-selective luminescence can be used as a probe to gather information on the site occupation and local surrounding of the Nd$^{3+}$ ions. Figure 5 shows the emission spectrum due to the $^4$I$_{9/2}$ multiplet at 10 K for two different excitation wavelengths.

Clearly, at least two different sites must be present to account for the observed emission spectra. As europium occupies the two different Ca sites in Ca$_2$SiS$_4$, it is not unexpected that the Nd ions also occupy both sites. Figure 6 shows the excitation spectra obtained at 10 K for the emission at 891 and 902 nm, along with the excitation spectra for the yellow and the red Eu$^{2+}$ emission bands. The excitation spectra largely coincide with the excitation spectra for the Eu$^{2+}$ emission bands, meaning that efficient energy transfer occurs from Eu$^{2+}$ to Nd$^{3+}$. Furthermore, the excitation spectra obtained for the Nd$^{3+}$ emission at 891 and 902 nm strongly matches the excitation spectrum for the yellow and the red Eu$^{2+}$ emission band, respectively, which is especially noticeable in the 550–600 nm region. Consequently, the Nd$^{3+}$ ions not only occupy two different sites, but they are also in close proximity to the europium ions. If this were not the case and the energy transfer took place via a long-range interaction, then the excitation spectrum for both Nd$^{3+}$ sites would be identical, apart from minor changes in the position of the direct transition to the $^4$G$_{5/2}$ state.

**The energy-level scheme.**—Recently, energy-level schemes have been presented in literature for persistent phosphors with various compositions. Although quite a bit of information on energy-level location can be derived from measurements on optical absorption, (photo)luminescence, thermal quenching, glow curves, etc., unifying
these data into an accurate energy-level scheme is far from straightforward. This is partly due to the complexity of the involved processes, such as the lattice relaxation after trapping of carriers and the uncertainty in the nature of the trap states.

To construct an energy-level scheme appropriate for Ca$_2$SiS$_4$: Eu, RE, we require the following data:

1. By analyzing the emission and excitation spectra, the location of the Eu$^{2+}$ energy levels can be estimated. Preferably, the configurational coordinate model is applied, which includes the effect of the lattice relaxation after photon absorption and emission and is related to the Stokes’ shift. To determine the lowest excited state of the $^4$F$_{j}$ multiplet of the 4f$^{6}$ configuration, the mirror-image relationship can be used.

2. The thermal-quenching behavior of Ca$_2$SiS$_4$:Eu$^{2+}$ provides the activation energy from the (relaxed) 5d state of Eu$^{2+}$ to the conduction band. The thermal-quenching temperature ($T_{0.5}$) is about 445 K for the yellow emission band and 470 K for the red emission, with some error caused by the strong overlap between the bands at these high temperatures. Using Dorenbos’ estimation method, the relaxed 5d states of the yellow- and red-emitting Eu$^{2+}$ centers should be positioned at about 0.65 and 0.70 eV below the conduction band, respectively.

3. The absolute position of the energy levels of the codopants in their divalent state can be estimated using the procedure described in Ref. 17 by determining the charge-transfer energy (CTE). As Dorenbos argued, this energy correlates with the energy difference between the top of the valence band and the RE$^{2+}$ ground state. The diffuse reflection was measured for undoped Ca$_2$SiS$_4$ and Ca$_2$SiS$_4$:RE (RE = Sm, Dy, and Nd) powders (Fig. 7). From the steep decrease in the reflection around 250 nm, the bandgap of Ca$_2$SiS$_4$ is estimated at 4.9 eV by comparing with the behavior of CaGa$_2$S$_4$:RE and using similar arguments to those used by Bessière et al. Note that the undoped Ca$_2$SiS$_4$ sample shows considerable absorption below the energy gap, which could be related to the presence of (intrinsic) defects. By subtracting the reflection spectrum for undoped Ca$_2$SiS$_4$, the CTEs for Nd, Dy, and Sm doping were determined at 4.2, 4.1, and 3.2 eV, respectively. For Sm and Dy doping, a single absorption band due to the charge-transfer transition was observed, while Nd doping introduces additional absorption bands besides the one at 4.2 eV. These CTEs are somewhat lower than the ones obtained by Garcia et al. in rare-earth-doped CaGa$_2$S$_4$. Nevertheless, the same trend between the rare-earth ions is observed, due to the shielding of the 4f electrons from the crystal field.

4. The thermal energy required to get persistence luminescence can be estimated from the TL glow curves. Obviously, this is far from straightforward, as multiple trap depths are observed, leading to overlapping peaks in the glow curves. Using Chen’s method, the trap depth for the main peak in the TL glow curves of Ca$_2$SiS$_4$:Eu is estimated at 0.3 eV. Codoping with Nd$^{3+}$ introduces other traps with different energy (Fig. 4) as the TL glow curves are further complicated. Generally speaking, the glow curve for the yellow center is shifted to a higher temperature compared to the one for the red emission center.

Compiling all this information, an energy-level scheme can be proposed (Fig. 8). The activation energy of the thermal quenching positions the lower 4f$^{5}$5d excited states with respect to the bottom of the conduction band. Based on the emission and excitation spectra, the 4f$^4$ ground state of Eu$^{2+}$ can be plotted as well as the higher 4f$^6$5d excited state. With this information, it is clear that energy transfer upon excitation of the yellow emission center to the red emission center can occur. The excitation spectrum is rather similar for both centers in the wavelength range of 270–360 nm. This could again point to energy transfer and puts some error on the absolute location of the higher Eu$^{2+}$ excited state for both centers.

Nevertheless, the exact location is not important in view of the mechanism for the persistent luminescence presented here. Note that excitation of the luminescence in Ca$_2$SiS$_4$:Eu$^{2+}$ is not efficient via the higher 4f$^5$5d excited state (Fig. 3), which can be related to the fact that this state is well within the conduction band of Ca$_2$SiS$_4$.

In the previous paragraphs, an accurate description was presented for the steady-state luminescence processes involved in Ca$_2$SiS$_4$:Eu$^{2+}$. To explain the persistence luminescence, the model...
should incorporate the following: (i) the observation of multiple trap depths, centered on an activation energy of 0.2–0.4 eV but slightly different for the yellow- and red-emitting centers (Fig. 4), (ii) excitation of the persistent luminescence via the higher 4f^5d excited states (Fig. 3), and (iii) the proximity of Nd^{3+} codopants and Eu^{2+}. In Fig. 8, two possible scenarios are presented. Traps T_1 are positioned by subtracting the activation energy for the persistent luminescence from the position of the bottom of the conduction band. T_1 is positioned slightly further away from the conduction band for the yellow emission center due to the high-temperature shift of the glow curve for this center. At first sight, requirements i and ii appear to be fulfilled. The disadvantage of this position is that the conduction-band levels are required to allow the recombination between the trapped electron and the Eu^{3+} ion. Hence, the thermally released electrons could also recombine with other (nearby) Eu^{3+} ions. In this way, the glow curves of both emission centers should be similar, which is not the case. Consequently, requirement ii is not fully met. One solution is putting the trap levels below the lower 4f^5d excited states, at positions T_2. This now fully “localizes” the trap levels to both emission centers. However, this would imply the possibility of filling the traps upon excitation via the lower 4f^5d excited states, which is in contradiction with requirement ii (Fig. 3). In the case of CaSiS_2:Eu,Nd, the position of T_1 and T_2 should not be considered fixed. From the glow curves (Fig. 4) it is clear that multiple trap depths are present. Hence, positions T_1 and T_2 should be seen as the barycenter of trap states with different energy.

An alternative energy scheme based on the configurational-coordinate concept is presented in Fig. 9. This level scheme is similar to Fig. 8, except that the effect of lattice relaxation after absorption and emission is taken into account. After excitation to the lower 4f^5d excited states (arrow 1), the system relaxes to the bottom of curve L, after which emission (arrow 2) can occur. With this model, the Stokes’ shift is explained. The width of the first excitation band is related to the excitation to the 4f^6 configuration. Excitation to the higher 4f^5d excited states (arrow 3) leads to nonradiative relaxation (arrow 4) to the bottom of curve L, after which emission can occur (arrow 2). To describe the persistent luminescence, curve T is introduced. After excitation to the higher 4f^5d excited states (arrow 3), an electron can be trapped and an Eu^{3+} ion is left behind. The entire system relaxes to the nearest neighbors (sulfur atoms in the case of CaSiS_2) move inward to the europium ion. Upon recombination between the Eu^{3+} ion and the trapped electron, an activation energy is required (arrow 5), after which luminescence can occur (arrow 2). Note that direct recombination (arrow 6) is not allowed, as this would lead to an emission spectrum deviating from the steady-state emission.

With this model, both requirements i and ii are fulfilled. Indeed, curves T and H have a crossover near the minimum of H, while the persistent luminescence cannot be excited via the lower 4f^5d excited states, as the crossover between L and H is energetically too far away from the minimum of L. The recombination is localized, without involvement of the conduction band. In this way, different glow curves can be present for the two emission centers. Indeed, the activation energy from the trap state(s) to curve L is different for both emission centers (Fig. 9). Again, based on the glow curves for CaSiS_2:Eu,Nd, multiple trap energies are present, and several curves with slightly different activation energy should be drawn around curve T.

The nature of the traps.—A more difficult topic to address is the nature of the traps involved in the persistent luminescence. CaSiS_2:Eu by itself already shows some persistent luminescence. Consequently, traps related to intrinsic defects must be considered. Codoping with certain RE^{3+} ions (e.g., Nd^{3+} and, to a lesser extent, Dy^{3+}) considerably enhances the persistent luminescence in CaSiS_2:Eu, while other codopants (e.g., Sm^{3+}) suppress the persistent luminescence. The role of the codopants might be dual, as they can introduce additional energy levels or create specific defects.

The introduction of trivalent rare-earth ions on the Ca^{2+} lattice sites is expected to create defects for charge compensation. Based on the site-selective luminescence in CaSiS_2:Eu,Nd, we conclude that the Nd^{3+} and Eu^{2+} ions must be in close proximity; hence, we can expect that the charge-compensating defect is also in the vicinity of the Eu^{2+} ion. For similar oxide materials, such as the aluminates, the presence of an oxygen vacancy was proposed. Although sulfides are known to be often sulfur-deficient, more research is required to establish the nature of the charge-compensating defects.

Besides charge-compensating defects, the incorporation of rare-earth ions also introduces additional energy levels. Dorenbos recently proposed a method to position the energy levels of all the lanthanide ions in the band structure of any host material. This method has proven (at least in a semiquantitative way) to be useful to explain thermal quenching, the depth of electron and hole traps, and the (in)stability of certain valence states. Until now, it has been tested mainly in oxide compounds, with, e.g., an excellent match between the model and the experimentally recorded glow curves of YPO_4:Ce^{3+},RE. For sulfide compounds, the method needs to be somewhat adjusted due to the large polarizability of the sulfide ion and its larger size compared to oxygen. Based on the position of the ground-state energy levels of Nd^{3+}, Dy^{3+}, Sm^{3+}, and Eu^{3+} (as derived from the CTE), we can expect the ground state of Pr^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} to have a similar separation from the bottom of the conduction band to Nd^{3+} (within a range of 0.3 eV). For CaSiS_2:Eu^{2+}, Dy^{3+}, we indeed find a considerable enhancement of the persistent luminescence compared to CaSiS_2:Eu^{2+} (Fig. 1). Sm^{3+} and, presumably, Tm^{3+} have their ground state much deeper in the bandgap (by about 1 eV compared to Nd^{3+}) and, indeed, they show an almost negligible persistent luminescence. Future work could include a completion of the RE series as codopant in CaSiS_2:Eu to test Dorenbos’ model, as it has been challenged recently.

Based on the model, only Ce^{3+} could act as a hole trap in CaSiS_2, while for the other rare-earth ions electron trapping is expected.

Conclusions

In this work, we showed the possibility of persistent luminescence in rare-earth codoped CaSiS_2:Eu. For the codopants studied, neodymium yields the strongest afterglow. The emission and excitation behavior of the persistent and the steady-state luminescence were compared. It was shown that the persistence emission is dominated by a band at 660 nm, giving the powder a deep-red appearance. The persistence emission can effectively be excited by wavelength shorter than 360 nm. An energy-level scheme based on the configurational-coordinate concept was presented to explain the experimental observations.
For (safety) sign applications, it appears that Ca$_2$SiS$_4$:Eu is not well suited for two reasons. First, the (photopic) eye sensitivity is relatively low for the red emission band in Ca$_2$SiS$_4$:Eu. For the low emission intensities encountered during the afterglow, the (scotopic) eye sensitivity is even lower, so that the persistent luminescence is easily measurable, although hardly visible.\textsuperscript{25,26} Nevertheless, considerable progress can be expected by optimizing synthesis conditions to alter the defect structure (e.g., the concentration of sulfur vacancies, the incorporation of the codopants, etc.). Second, the material requires excitation below 360 nm for the persistent luminescence to occur, which makes it less attractive as it cannot be charged by standard artificial light sources.

However, applications could emerge in other fields. For instance, it was recently shown that the (near-infrared) persistent material Ca$_{0.2}$Zn$_{0.9}$Mg$_{0.9}$Si$_2$O$_6$:Eu,Dy,Mn can be used as a nanoprobe for in vivo imaging,\textsuperscript{27} with several advantages over other fluorescence imaging techniques. The (red) emission band in Ca$_2$SiS$_4$:Eu,Nd nicely overlaps with the tissue transparency window, allowing the persistent light emission to be detected.

Finally, this material could hold the key to some unsettled questions in the field of persistent luminescence. Due to the presence of two distinct emission centers, the storage and release model has to be compatible with the observations of TL and persistent luminescence for both emission centers. In the present work, we have already made important suggestions such as the close proximity of the emission center (Eu$^{2+}$) and the traps (Nd$^{3+}$ and other defects) and the role of the conduction band. Specific research (e.g., using X-ray absorption fine structure) is currently planned to verify these assumptions.

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