



## Persistent luminescence in nitride and oxynitride phosphors: A review



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### ABSTRACT

The research field of persistent luminescence has experienced a strong growth in the past two decades, with a steady development of new materials and applications. Here we give an overview of the recent progress in a specific class of host materials, namely oxynitride and nitride persistent phosphors. These are interesting hosts to explore because of their unique characteristics, such as chemical stability and tunability of the emission over the entire visible range upon doping with divalent europium. To yield persistent luminescence however, co-dopants have to be added or the synthesis conditions have to be adjusted. Specific materials, such as  $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu,Tm}$  and  $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}$ , are highlighted and their properties are put into the context of emerging applications such as in vivo imaging and pressure sensing via mechanoluminescence. Finally, directions for future research are given.

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### 1. Introduction

Persistent luminescence is a specific type of photoluminescence for which the emission is delayed by minutes, hours or even days after the excitation has ended. This process is most often temperature dependent and is also called afterglow or long-lasting phosphorescence (LLP) [1,2].

Although the first persistent phosphor was already scientifically described four centuries ago [3], dedicated research into this class of materials only geared up after the discovery of strontium aluminate doped with europium and dysprosium ( $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ ), now 20 years ago [4,5]. Since then, many new phosphor materials have been reported [6,7], which can be roughly divided into two groups. The first group is based on the use of divalent europium as luminescence center, often with other rare earth ions as co-dopants. The most studied materials in this group are  $\text{CaAl}_2\text{O}_4:\text{Eu,Nd}$  [8,9],  $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu,Dy}$  [10],  $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$  [5,11] and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu,Dy}$  [12]. An extensive overview is given in the review by Van den Eeckhout et al. [7]. The second group contains non-rare earth ions (such as  $\text{Mn}^{2+}$  [13] or  $\text{Cr}^{3+}$  [14–16]) or other rare earth ions (such as  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Tb}^{3+}$ ) as luminescence centers. A recent overview on the members in this second group can be found in [6].

In general terms, the first step in the process of persistent luminescence is the liberation of charge carriers upon illumination at

specific wavelengths. These are subsequently trapped at defects, which are intrinsically present in the material or which were intentionally introduced. By thermally assisted detrapping or quantum tunneling effects, the charges can then move to a recombination center to yield the delayed luminescence [17–19]. Several aspects of this trapping and detrapping process in persistent phosphors are still under debate, mainly on the (chemical) nature of the traps and the trapping/detrapping pathways [20,21]. Consequently, the optimization of persistent phosphors and the discovery of new ones is often still a matter of trial-and-error.

Next to the efforts towards unraveling the mechanism behind persistent luminescence, there are two driving forces steering the research and development of persistent phosphors. First of all, there is an interest to extend the more traditional applications areas (such as emergency signage, watch dials toys and gadgets), by increasing the brightness and decay time. This would allow night-long emission with sufficient brightness, for instance for use as glow-in-the-dark roadmarks.

Secondly, the current gamut of emission colours is mainly limited to the blue and green part of the spectrum. The development of red emitting materials is required for extending the colour range of glow-in-the-dark signage used in emergency situations. The low eye sensitivity for red light, especially under low light conditions, puts strong demands on the brightness of these phosphors [22,23]. Emission in the deep red part of the visible spectrum or in the near-infrared are desired for surveillance applications [24] and in vivo bio imaging [25,26].

In this paper we give an overview of the present state-of-the-art for persistent luminescence in oxynitride and nitride hosts, and

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discuss their usefulness in the for the abovementioned applications. The discussed compounds are given in Table 1. For the afterglow duration, we take the convention of using the 0.32 mcd/m<sup>2</sup> threshold, similar to the procedure used in industrial testing [27]. This threshold is about 100 times the visibility threshold of the dark adapted human eye.

Unfortunately, it appears that the afterglow duration is sometimes determined without making absolute intensity measurements but by observing the sample with the dark adapted human eye, until dropping below the visibility threshold. This duration is then matched with the 0.32 mcd/m<sup>2</sup>, which obviously compromises the objective comparison of different reports or different persistent phosphors. A complication is that the eye sensitivity curve shifts to shorter wavelengths for low light intensities, as encountered in the mesopic or scotopic range [23]. Therefore, absolute measurements (even in radiometric units in the case of long wavelength emission [24]) are advisable, preferably also with clear specifications of the excitation conditions (spectral distribution, duration and intensity).

## 2. Overview of nitride phosphors

Eu<sup>2+</sup> doped nitride phosphors are key to achieve low colour temperature, high colour rendering and high efficiency in phosphor-converted white LEDs [44,45]. Although the combination of a blue pumping LED and a yellow YAG:Ce phosphor readily produces white light with high colour temperature, the emission lacks in the red part of the spectrum. To achieve lamps with colour temperature in the 3000 K range and a high colour rendering index, a second phosphor is required. The red phosphors should preferably have a relatively narrow emission band and a peak wavelength not higher than 625 nm, otherwise the human eye is not sensitive enough for the emitted light and the efficiency of the LED is compromised [46]. When using Eu<sup>2+</sup> as dopant ion, this can in general only be achieved in certain sulfide (e.g. Ca<sub>1-x</sub>Sr<sub>x</sub>S:Eu) or nitride hosts [47,48]. The latter materials are commonly preferred, due to stability issues with sulfides [49] and a better thermal quenching behaviour. Several high performance nitride materials have been developed, such as Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu, Ba<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu, CaAlSiN<sub>3</sub>:Eu and SrAlSiN<sub>3</sub>:Eu (including solid solutions to obtain spectrally optimized phosphors) [50–53]. The research on persistent phosphors has taken advantage of these developments, with the M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu compositions getting attention.

Miyamoto et al. and Van den Eeckhout et al. independently reported on the persistent luminescence in Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu and the influence of especially co-doping with Tm<sup>3+</sup> to increase the afterglow intensity [30,32]. The afterglow duration of Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu

without co-dopants was found to be only 150 s, taking 0.32 mcd/m<sup>2</sup> as threshold. This was related to a thermoluminescence peak around 350 K, albeit with low intensity due to a limited number of traps [31]. The afterglow duration increases to 2500 s upon appropriate codoping with thulium [27]. The addition of thulium introduces new traps, which are observed in the thermoluminescence glow curves around 220 K (which is of no use for afterglow at room temperature) and 350–375 K [30,32]. Next to these glow peaks, a very shallow intrinsic trap is found in all Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu,RE phosphors, with release at 110 K in thermoluminescence [30,32]. The addition of Dy or Nd to Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu does introduce additional traps, but these are too shallow to play a role at room temperature [30,32]. The deeper trap observed at 350–375 K was related to isolated Tm<sup>3+</sup> ions or to Tm<sup>3+</sup>–Eu<sup>2+</sup> pairs at the Ca<sup>2+</sup> site(s) [30]. It was observed that the concentrations of europium and thulium have to be fairly low (in the range from 0.5% to 1% substitution of Ca) [27,30]. The persistent luminescence can be influenced by variations in the Ca:Si stoichiometry, and by addition of Li [27,28,30].

Maldiney et al. showed that Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu, Tm can effectively be used for in vivo imaging of small animals, by following the afterglow of nano-sized Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu,Tm particles which were excited just before injection [26]. Although the emission spectrum of Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu,Tm is at the edge of the tissue transparency window, imaging could still be performed. A top-down approach was used to obtain nano-sized particles, involving pulsed laser ablation or wet grinding, followed by size selection [26]. The rather complex synthesis conditions for the M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu do not easily allow a bottom-up synthesis method to obtain nano-sized particles with a priori specified size distribution.

The choice of surface functionalization (for instance with PEG (polyethylene glycol)) was shown to improve the distribution and keep the particles in the blood stream [26]. It also allows to tune the target specificity. Although Ca<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu,Tm has the advantage that it can be recharged by irradiation with visible light after injection [31], the afterglow intensity is at the moment not sufficiently high to allow monitoring for extended periods, in contrast to recently reported Cr<sup>3+</sup> persistent phosphors, which in addition have a more suited emission spectrum [15].

For Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu, Teng et al. reported the persistent luminescence afterglow time to be 150 s, extending to 600 s upon co-doping with Tm<sup>3+</sup> [33], which is slightly longer than results described in [27]. Unfortunately, the traps relevant for the afterglow cannot be filled upon excitation with visible light (i.e. by excitation into the lowest 5d excited states of divalent europium) [31], hampering several applications. Wang et al. reported persistent luminescence in SrCaSi<sub>5</sub>N<sub>8</sub>:Eu,Tm, having a broad emission (FWHM of 120 nm) peaking at 647 nm, similar to the steady state photoluminescence [34]. The peak wavelength of the solid solution is red-shifted

**Table 1**  
Key data for (oxy)nitrides showing persistent luminescence.  $\lambda_{\max}$  is the wavelength of the afterglow emission peak, FWHM is the full width at half maximum. Excitability refers to the possibility to induce persistent luminescence by visible light (+: good; T: temperature dependent; -: poor; ?: not reported). Afterglow duration ((\*) to 0.32 mcd/m<sup>2</sup>; (o): observed by naked eye).

| Material  | Dopant(s) | $\lambda_{\max}$ (nm) | FWHM (nm) | Excitability | Afterglow (s)       | Ref.       |
|---|-----------|-----------------------|-----------|--------------|---------------------|------------|
| Ca <sub>2</sub> Si <sub>5</sub> N <sub>8</sub>    | Eu        | 615                   | 92        | +            | 150 (*) – 1200 (o)  | [26–32]    |
|   | Eu,Tm     |                       |           |              | 2500 (*) – 3600 (o) |            |
| Sr <sub>2</sub> Si <sub>5</sub> N <sub>8</sub>    | Eu        | 625                   | 88        | –            | 80–150 (*)          | [27,33]    |
|   | Eu,Tm     |                       |           |              | 190–600 (*)         |            |
| SrCaSi <sub>5</sub> N <sub>8</sub>                | Eu,Tm     | 647                   | 120       | ?            | 1800 (*)            | [34]       |
| Ba <sub>2</sub> Si <sub>5</sub> N <sub>8</sub>    | Eu        | 585                   | 93        | T            | 400 (*)             | [27,31,35] |
| g-C <sub>3</sub> N <sub>4</sub>                   | None      | 553                   | 175       | +            | 4800 (o)            | [36]       |
| CaSi <sub>2</sub> O <sub>2</sub> N <sub>2</sub>   | Eu        | 506                   | 106       | –            | 400 (*)             | [37]       |
| SrSi <sub>2</sub> O <sub>2</sub> N <sub>2</sub>   | Eu        | 539                   | 76        | –            | 6000 (*)            | [37,38]    |
| BaSi <sub>2</sub> O <sub>2</sub> N <sub>2</sub>   | Eu        | 498                   | 32        | +            | 2800 (*)            | [37,39–41] |
| BaAlSi <sub>5</sub> N <sub>7</sub> O <sub>2</sub> | Eu        | 515                   | 125       | –            | 2400 (o)            | [42]       |
| BCNO  | None      | 520                   | 90        | +            | 7200 (o)            | [43]       |

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