

Design, Synthesis and Luminescence Study of Rare Earth Doped Persistent Phosphor

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Abstract-

Owing to the unique mechanism of photoelectron storage and release, long persistent phosphorescence, also called long persistent luminescence or long lasting afterglow/phosphorescence, plays a pivotal role in the areas of spectroscopy, photochemistry, photonics and materials science. Persistent luminescence, the phenomenon whereby a luminescent materials keeps emitting light after the excitation has stopped, has intrigued people since centuries. In this review, we present afterglow mechanisms, materials system, and applications of LPPs. We present the possible mechanisms, which involve the variation of trap distribution during the trapping and de-trapping process, complicated photo-ionization reaction of trap site levels and impurity centers together with their corresponding migration kinetics of carriers. Meanwhile, we emphasize the characterization techniques of defects, used to qualitatively or quantitatively describe the types, concentrations and depths of the traps. This review article also highlights the recent advances in LPPs materials with a focus on the LPPs' hosts and optically active centers as well as their control, tuning and intrinsic links. We further discuss the classification of LPPs based on the different emission and excitation wavebands from the ultraviolet to the near-infrared region along with an overview of the activation mode of afterglow.

Introduction

Persistent luminescence is an intriguing phenomenon that has fascinated people for a long time. It is defined as the long afterglow, sometimes erroneously called phosphorescence, present after the excitation of a luminescent material has stopped. Persistent luminescent materials are commonly called glow-in-the-dark phosphors, though not all materials giving off light for a long time without external excitation can be classified as persistent phosphors. Indeed, many living organisms such as glow worms, fireflies, sea sparkle (*Noctiluca*

scintillans), some deep-sea fish, and fungi emit light, based on a (bio) chemical reaction, a phenomenon called chemi-luminescence or more precisely, in living organisms, bioluminescence. Similarly, it is a common misconception among laymen that radioactive compounds show glow-in-the-dark persistent luminescence.

The persistent luminescent compounds consist of an inorganic host matrix doped with luminescent ions and, just like in non-persistent phosphors; the emission spectrum is determined by the combination of the intrinsic energy levels of the dopant ions and their interaction with the host lattice. When transition metal ions such as Cr^{3+} or Mn^{4+} are used, this electron–phonon and electron–ligand interaction is quite strong, and the dominant emission wavelength can be tuned to some extent. Rare earth ions are by far the most popular dopants in phosphors; for most of them, the emission stems from 4f–4f transitions that are well-shielded from the crystallographic environment and lead to sharp emission features with roughly constant wavelengths, independent of the host crystal into which they are incorporated. Notable exceptions are Ce^{3+} , Yb^{2+} , and Eu^{2+} , showing 5d–4f transitions in many hosts, which can be tuned over a broad wavelength range. Specifically, Eu^{2+} is the “workhorse” of persistent phosphors, and the best performing persistent luminescent materials known to date are Eu^{2+} -based: $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$, developed by Matsuzawa in 1994^{6,7} and ubiquitous as a green emitter in emergency lighting, safety signs, and toys, $\text{CaAl}_2\text{O}_4:\text{Eu,Nd}$ as a violet-blue emitter, and $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu,Dy}$ as a blue persistent phosphor. High performance red-emitting persistent phosphors are more scarce, not in the least because the eye sensitivity shifts to shorter wavelengths at low illumination levels, making the eyes less sensitive to red light.^{8–10} As an illustration, Fig. 1 shows the normalized phosphor output during and after illumination with a blue LED, for the “normal” phosphor $\text{YAG}:\text{Ce}$ ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$), having a very fast response and decay, and the benchmark persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$.

In all cases and this is the essential difference between an “ordinary” phosphor with a decay time in the range of nanoseconds to milliseconds and a persistent phosphor—the phenomenon of persistent luminescence relies on the existence of metastable trap levels that can temporarily store the excitation energy. In some cases, these trap levels are due to native defects, such as oxygen vacancies, but often, co-dopants like Nd^{3+} or Dy^{3+} in the abovementioned cases, are used to introduce these trap levels.

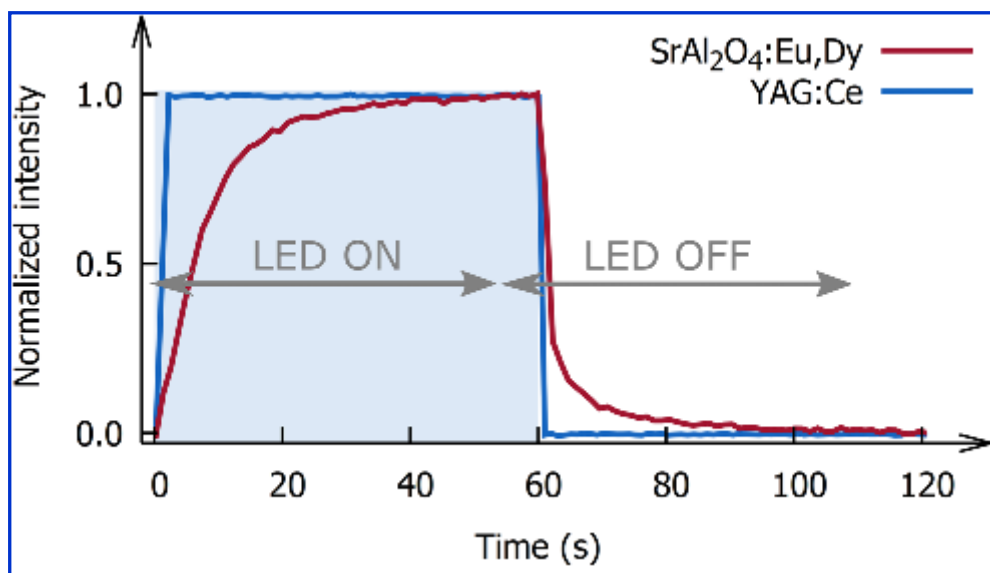


Fig.1. Normalized emission from a “normal” phosphor YAG:Ce ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) and the persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ during and after excitation with a blue LED.

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Most persistent phosphors can be excited using x-rays (Radioluminescence or RL), electrons (cathodoluminescence or CL), or UV/visible light (photoluminescence or PL). In all these cases, the persistent phosphor is showing “ordinary” luminescence with a short decay time, but at the same time, charge carriers are transferred from the activator to the traps and the traps are gradually filled. If the phosphor is illuminated for a sufficiently long time, a dynamic equilibrium of trap filling by the illumination and emptying traps by thermal excitation and optically stimulated luminescence (OSL) sets in. If the excitation is stopped after this charging phase, the traps are slowly emptied by the thermal energy, available at room temperature, and energy can be transferred back to the dopant ions. This leads to strongly delayed luminescence, with a decay time up to hours, depending on the depth of the traps and the ambient temperature.

Finally, the phosphor performance also depends on the type of excitation source used. For instance, many persistent phosphors are easily chargeable in the UV, while excitation at longer wavelengths is often not efficient to fill traps, due to the presence of (thermal) energy barriers for the trapping process. Hence, it is important to always specify in detail the type, spectral output, and intensity of the excitation source. Preferably, those parameters are chosen to mimic the intended application. For instance, excitation with orange or red light is more sensible than using UV radiation in the case of in vivo bioimaging applications

A persistent luminescent material emits light without using an external power source such as a battery. Instead it uses energy stored inside the material itself. The best-known applications are decorations, toys, safety signage, watch dials and displays (Figure 2) [3]. Except for the safety signage applications used in airplanes and public buildings to guide people to the nearest emergency exit in case of a power failure, the listed applications are often 'gadgets' where the persistent luminescence is a gimmick rather than an added value. However, persistent luminescent phosphors are recently the subject of other fields of applications. For example, the use of red or near infrared emitting persistent luminescent nano-particles for in vivo medical imaging is investigated. Another example is the development of domestic lighting. Whereas persistent luminescence was usually seen as a disadvantage for a conversion phosphor in LEDs, it is now gaining some popularity in the development of phosphor converted AC-LEDs. In this type of LEDs, conversion phosphors with a certain amount of afterglow might be beneficial to reduce the intrinsic flickering of the LED when driven by an AC source [8, 9]. Note that the time scale of the persistent luminescence needed in this application is of the order of tens of milliseconds, rather than minutes to hours. Also the use of persistent luminescent materials in trace markings has been proposed before and recently this idea became a hot topic in worldwide news when a Dutch artist/designer tried to realize this application in a field test.

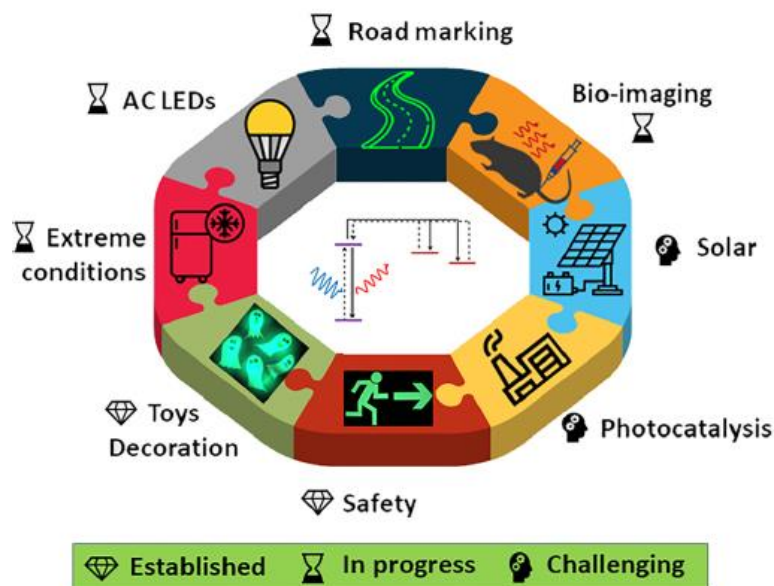


Fig. 2 Overview of reported or potential applications of persistent phosphors. Details on the different applications are found in the text.

Persistent phosphors are perhaps best known for their use in a variety of objects such as toys, watches, and wall decorations. They are only incorporated into these objects to provide them with a glow-in-the-dark feature and as such they are not essential to the workings of these applications. However, in other applications, persistent phosphors are indispensable for a flawless operation and consequently these applications impose more stringent requirements with respect to initial brightness and duration of the phosphor's afterglow. An example of a successfully commercialized application that fully relies on the afterglow of persistent phosphors is the glow-in-the-dark safety signage in buildings and airplanes. In this case, the use of a persistent phosphor ensures that the safety signage remains visible, even in the case of a power outage.

In addition to the widespread use of persistent phosphors in toys and safety signage, many new applications are being proposed every year. The list of possible applications includes the use persistent phosphors in glow-in-the-dark road markings, for bioimaging, for photocatalysis, to reduce flickering in AC-driven LEDs, as pressure sensors or to visualize ultrasound beams.

Although the best persistent phosphors are fit for common safety applications, where emergency signage should typically remain visible for one hour after power stoppage, the storage capacity does not yet allow to bridge a full night, hampering the application in road markings. In contrast, similar application areas have been proposed, such as glow-in-the-dark bicycle paths, where the light emission is not absolutely vital, but offers additional guidance. The absolute decay luminance of the same exit sign as pictured in Fig. 3 together with the benchmark luminance, attained after 27.5 h.



Fig. 3. Photographs of a commercial glow-in-the-dark emergency exit sign, taken at different times after excitation and using different camera settings. The sign was charged using a black light lamp at 365 nm during 10 min

Fundamentals of persistent luminescence

Trap levels

The peculiar afterglow of persistent luminescent phosphors is the result of energy storage upon optical excitation. The reason why energy can be stored in an afterglow phosphor is related to the presence of traps in the material shown in Fig. 4. Traps are energy levels in the band gap of the phosphor's host lattice and in these states charge carriers can get trapped. The origin of the trap levels is presumably due to imperfections in the crystal lattice of the phosphor. These imperfections are assumed to be lattice defects, impurity ions, intentionally added codopants, Upon optical excitation of a luminescent center in the phosphor, the excited electron has a certain probability to escape and get caught by such a trap, leaving behind an ionized luminescent center and a filled trap. The trapped electron cannot recombine directly from the trap level, only by a small thermal activation it can be released and upon recombination with an ionized luminescent center light can be emitted. The requirement of thermal activation leads to trapped electrons being released slowly thus delaying the luminescence process. The activation energy required to release a trapped electron is provided by the available thermal energy. The speed by which traps are emptied depends on the trap depth and the temperature. If the trap level is located far below the conduction band we call it a deep trap and a considerable amount of thermal energy is needed to release the electron. Therefore, at room temperature, deep traps will take a very long time before they get emptied or will not be emptied at all. A trap level located close to the conduction band is called a shallow trap and only limited thermal energy is required to release the electron. At room temperature, shallow traps will be emptied almost immediately after they get filled or within a few seconds. The trap depth is usually expressed in eV below the bottom of the conduction band. Traps with a depth between the deep and the shallow traps we call useful traps, as those are responsible for the typical afterglow in a persistent luminescent phosphor. The performance of a persistent luminescent phosphor thus strongly depends on the depth of the traps in the phosphor.

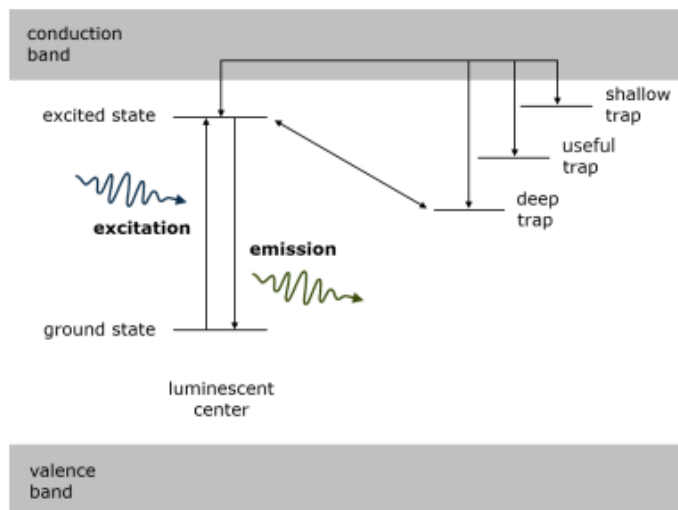


Fig. 4: Traps levels in the band gap of the host lattice can capture electrons from the excited luminescent centres. Since thermal energy is required to escape from these traps levels, the luminescence is delayed. The trapping and detrapping process might occur via the conduction band or directly by localized transitions.

To achieve efficient persistent luminescence at room temperature, the trap should have a specific depth which is neither too shallow nor too deep. If the trap is too shallow, the electrons will almost immediately be released. If the trap is too deep, the available thermal energy does not suffice to release any of the trapped electrons. According to literature it is often stated that a trap depth around $0.6 - 0.7\text{eV}$ is ideal to achieve efficient persistent luminescence at room temperature, although this also depends on the attempt to escape frequency (the so-called frequency factor). However, rather than a single trap level, the trap system in a persistent luminescent phosphor presumably consists of a continuous distribution of traps depths. The shallow part of this distribution empties faster and provides the initial intense, but fast decaying, afterglow while the deeper part of the trap distribution empties slowly and thus causes the low afterglow intensity after some time. It is important to notice that the terms 'shallow' and 'deep' are not strictly defined. They are related to the available thermal energy and thus dependent on the temperature of the phosphor. For instance, upon increasing temperature, part of the deep traps (as labelled at room temperature) become useful traps as the probability of releasing electrons from these traps will increase.

A good knowledge of the trap system in a persistent luminescent phosphor is one of the key elements in understanding the mechanism behind persistent luminescence or in developing new persistent luminescent phosphors. Characteristics of persistent luminescence a typical intensity role of a persistent luminescent

phosphor during and after optical excitation at room temperature is shown in Figure 1.3. During the excitation phase, the luminescence intensity of the persistent luminescent phosphor does not immediately reach its maximum value as is the case for a regular phosphor. Instead, it increases gradually during several seconds or minutes until a saturation value is reached. During this initial phase, which we will call the charging phase, several processes are at play: PL emission, trapping and afterglow emission. When the optical excitation of the persistent luminescent phosphor is ended, no more activators are excited by incoming photons. However, in contrast to a regular PL phosphor, the luminescence does not vanish immediately since traps are still being emptied, leading to recombination at the luminescent.

Charging

Besides investigating the duration of the afterglow and the shape of the afterglow curve, also the charging behaviour (i.e. the build-up in emission intensity upon excitation) of a persistent luminescent phosphor is sometimes the subject of research. As described above, upon charging, the emission intensity of a persistent luminescent phosphor increases gradually during several seconds or minutes until a saturation value is reached. This is due to the interplay of several processes: PL emission, trap filling and afterglow emission. The combination of these processes defines the shape of this charging curve. As it is already difficult to model or and a closed expression for the afterglow, modelling the charging curve of a persistent luminescent phosphor is even more complicated, as it involves afterglow emission from a continuously filling trap or trap distribution. In some cases, the charging behaviour can be fitted using a mathematical expression. However, this is of little meaning if there is no solid physical background to this expression.

Thermoluminescence

A good knowledge of the trap system in a persistent luminescent phosphor is important to understand the mechanism behind persistent luminescence. A technique often used to investigate the depth of traps in materials is thermoluminescence (TL). It is a versatile tool that is not only used to investigate persistent luminescent phosphors, but also for dosimetry and geological dating purposes. The term thermoluminescence is somewhat unfortunate since it sounds as if the heating is the main energy source of the luminescence, while actually an initial excitation is the source of energy and the heating is only a trigger to release the stored energy from the material. Thermally stimulated luminescence would be a more descriptive term, however, thermoluminescence is traditionally more often used and popularly accepted [29]. The principle of a classic

TL measurement is shown schematically in Figure 1.5. First the material of interest is excited for a certain time, using ionizing radiation, at low temperature (typically at room temperature). The material is then heated in a controlled way, usually with a constant heating rate, while the light output is continuously measured. When the recorded light output is plotted as a function of the temperature of the material we obtain a 'glow curve'. The appearance of a peak in the glow curve, usually called a glow peak, indicates the presence of a charge carrier trap in the material. The temperature at which the glow peak is located is a measure of the trap depth, since it is the temperature at which enough thermal energy is available for the trapped charge carriers to be released recombines at luminescent centres. A shallow trap gives rise to a glow peak at low temperature while a deep trap causes a glow peak at much higher temperature (figure 1.6). The shape, height and location of the peak all contain information on the number and depth of the involved trap(s). Although the TL technique is experimentally straightforward, extracting information about the traps in a material from a TL measurement is very complicated. For a given material, the glow peak might depend strongly on the nature of the initial excitation. For example, excitation with UV light may result in a different glow curve than that recorded following, or irradiation. Moreover, even when the same kind of excitation is used the appearance of the glow curve might depend on the excitation energy or on the excitation strength and duration. If it is already difficult to extract information about a single trap in a certain material, persistent luminescent phosphors complicate this even more. First of all, it is known that in many persistent luminescent phosphors a continuous trap depth distribution is present, rather than a few discrete trap levels, resulting in a very broad and difficult to model TL glow peak [13]. A second difficulty is related to the depth of the trap distribution in a persistent luminescent phosphor. As the afterglow of a persistent luminescent phosphor is a form of thermally stimulated luminescence, part of the trap distribution already empties or is empty at these temperatures. This implies that a TL glow peak recorded from room temperature only contains partial information about the trap distribution.

Mechanism - Phosphorescence lifetimes are usually longer than the lifetime of the excited state and depend on the trap depth and trapping/de-trapping rates. Fluorescence lifetimes, on the other hand, depend on the transition strength between the two states involved, which includes a ground state and an excited state only. Phosphorescence can be categorized by its lifetime as: Very Short Persistent Phosphorescence (VSPP) that has lifetime of the same order of magnitude as the lifetime of excited state, i.e. in the order of milliseconds, and it is associated with very shallow traps. Some examples are scintillators and display phosphors. Short Persistent Phosphorescence (SPP) that lasts for seconds and generally becomes noticeable to the human eyes.

Most phosphors show short persistent phosphorescence after they are exposed to the UV, visible light, plasma beam, electron beam or X-rays. Persistent Phosphorescence (PP) lasts for minutes and is due to the deep traps in the materials. These traps hold electrons or holes for some time and afterwards release thermally. Long Persistent Phosphorescence (LPP) shows lifetimes of the order of tens of minutes or hours. Although many new phosphors have been developed recently, only a few can be excited under natural light like sunlight. The issue of convenient excitation source is very important and actually limits the applications of long persistent phosphors. Many novel methods in the synthesis have been developed to produce persistent materials. These methods have mainly included, selective codoping with various ions to generate electrons or hole traps and defect related electron traps.

Objective (s) and Scope

Though several simple and efficient routes have been proposed for the synthesis of persistent phosphor, still there remain sufficient scope to improve the synthesis methods to achieve precise control over the particle size, morphology and distribution of phosphor particles impacting the luminescence properties for application in safety signage. The present work deals with the exploration of the blueprint for the rational design, solution synthesis and characterization of rare-earth doped oxide based nano-phosphors by various feasible experimental techniques. Rational design and solution syntheses of oxide based persistent phosphor doped by several trivalent rare-earth ions such as Ho^{3+} , Yb^{3+} , Er^{3+} , Eu^{2+} , Dy^{3+} . Phosphors will be significant thrust for the development of high quality phosphors with enhanced brightness, afterglow times and appreciable color purity. Blending of boric acid as a chemical flux along with rare-earth dopants has arisen as an effective way to enhance the photoluminescence intensity, crystallinity and efficiency of the phosphor. The addition of flux has a great influence on the ion diffusions in the reaction, particle size distribution, growth condition, crystallization process as well as the formation of target product matrix with good crystallinity. Study of the structural, morphological and optical properties of the rare-earth doped as-synthesized persistent phosphors. Study of the effect of concentration of the rare-earth ions as dopant, on the structural and photoluminescence properties of the synthesized persistent phosphors. Assessment of the effect of different synthesis methodologies like 'Complex based precursor solution method'; 'Co-precipitation technique' as well as 'Hydrothermal route' on the luminescence and TL properties of the persistent phosphors.

A brief review of the work already done in the proposed research work

A wide variety of host materials are used as luminescent compounds, but when it comes to persistent luminescence, the number of known hosts is relatively low. The majority of research on this phenomenon is concentrated around the aluminates, with SrAl_2O_4 as most famous representative, and the silicates, represented by $\text{Sr}_2\text{MgSi}_2\text{O}_7$. Besides these two main classes of materials, only few host crystals have been found to exhibit persistent luminescence with Eu^{2+} activators. These materials are often labeled as phosphorescent, but the definition of phosphorescence is rather ambiguous, since the term is also used for luminescence where a quasi-stable state is involved, causing an increased lifetime of the fluorescence decay. However, even the decay from such a quasi-stable state usually does not last longer than a second [3]. We are interested in materials where the afterglow is caused by the existence of suitable charge carrier traps in the crystal [11], and remains visible for a reasonable amount of time. The borderline between visible and invisible is not sharply defined, and neither does there exist a consensus on a reasonable amount of time. In this review, we will focus on materials that have an afterglow decay time longer than several minutes, where the decay time is defined as the time between the end of the excitation and the moment when the light intensity drops below 0.32 mcd/m^2 , roughly 100 times the sensitivity of the dark adapted human eye [12]. This is a definition similar to the one used in the safety signage industry, and by various researchers [13]. The data in the following tables are taken directly from the mentioned references. Only the codopants with the strongest positive influence on the afterglow are listed. Afterglow durations are meant to show the greater picture, and should only be seen as orders of magnitude. New persistent materials are continuously discovered. The following list therefore does not pretend to be exhaustive, but it does, to the best of our knowledge, include nearly every host material in which a significant Eu^{2+} -based afterglow has been reported.

Recently, $\text{Eu}^{2+}/\text{Dy}^{3+}$ co-doped alkaline-earth (Ba, Sr, Ca, Mg) aluminates host materials have attracted considerable attention as a new class of bright and long persistent luminescent phosphors for broad band emission area as well as these materials have been developed rapidly to replace the conventional sulfide afterglow materials. These rare earth doped strontium aluminates exhibit exceptional properties, such as higher luminescent intensity in visible region, higher quantum efficiency, longer lasting phosphorescence (or afterglow), excellent photo-resistant, and higher chemical stability. The long afterglow phosphor probe is associated with forensic, security signs, traffic signage, emergency route signs, and display applications. The Eu^{2+} ions doped phosphors provide typical emission bands from blue to red regions of the electromagnetic spectrum depending on the host lattice due to crystal-field effects. Moreover, the phosphorescence of dopant

Eu²⁺ ion in host lattice is caused by the dipole allowed optical transition from the lowest ⁴f₆⁵d₁ excited state to the ⁴f₇⁵d₀ ground state. The afterglow time and intensity of these LPL phosphors materials can be enhanced by co-doping with other rare earth ion Dy³⁺. These Eu²⁺/Dy³⁺ co-doped strontium aluminates phosphors exhibit a rapid decay from the Eu²⁺ ion followed by a long persistent due to the Dy³⁺ ion, which trap the holes that are associated with the lattice defects in the host material. The peak position of emission spectrum depends on the nature of emitter, while the afterglow intensity and duration time are also associated with the property of the trap. Thus, these prevailing virtues make the Eu²⁺/Dy³⁺ co-doped alkaline-earth aluminates a promising contender that lead to wide applications of the long persistent materials.

At present, the mechanisms responsible for persistent luminescence are not yet fully understood. Most authors agree on the general mechanism of charge carriers getting trapped in long-lived energy levels inside the band gap. Many details, however, remain unclear. For example, it is unknown whether these charge carriers originate from the luminescent centers, or if they are created directly by excitation from the valence or conduction band. Another obscurity is how the energy stored in these traps is conducted to the luminescent centers, by direct energy transfer, or through charge carrier transport in the conduction or valence band. The influence of codopants and lattice defects in the neighborhood of the activators is another unsolved issue. Future experiments are necessary to unravel these mysteries. The most promising techniques are the ones that were, until recently, often overlooked. Synchrotron radiation (such as XANES and EXAFS) and EPR measurements offer insight into the structure, composition, valence states and charge distribution of materials, and could provide an answer to these theoretical questions, answers that cannot be offered by photoluminescence and thermoluminescence experiments only.

Table 1. Known Eu²⁺ -based persistent luminescent aluminates.

Host material)	Dopants	Fluorescence maximum (nm)	Afterglow maximum (nm)	Afterglow duration
SrAl ₂ O ₄	Eu ²⁺ , Dy ³⁺	520 (green)	idem	>30 h
CaAl ₂ O ₄	Eu ²⁺ , Nd ³⁺	440 (blue)	430 (blue)	>5 h
BaAl ₂ O ₄	Eu ²⁺ , Dy ³⁺	500 (green)	idem	>2 h

$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$	$\text{Eu}^{2+}, \text{Dy}^{3+}$	490 (blue)	idem	>20 h
SrAl_4O_7	$\text{Eu}^{2+}, \text{Dy}^{3+}$	480 (blue)	idem	>3 h
$\text{SrAl}_{12}\text{O}_{19}$	$\text{Eu}^{2+}, \text{Dy}^{3+}$	400 (blue)	idem	>3 h
$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	$\text{Eu}^{2+}, \text{Nd}^{3+}$	440 (indigo)	idem	>10 min
$\text{Sr}_3\text{Al}_2\text{O}_6$	$\text{Eu}^{2+}, \text{Dy}^{3+}$	510/610 (disputed)	idem (disputed)	
$\text{SrMgAl}_{10}\text{O}_{17}$	$\text{Eu}^{2+}, \text{Dy}^{3+}$	460 (blue)	515 (green)	>3 min
$\text{BaMgAl}_{10}\text{O}_{17}$	$\text{Eu}^{2+}, \text{Co}^{3+}$	450 (blue)	idem	>5 min

Motivation of the work

Persistent luminescent research has a promising future. The search for new and better materials with Eu^{2+} ions as activators continues and has recently turned to other host materials, based on the developments in LED conversion phosphors. Additionally, the quest to unravel the mechanism behind the persistent luminescence has entered a new path. Various models have been proposed in the past few decades with only a small amount of experimental backup, but only recently researchers have started applying new and promising techniques that could confirm or disprove these theories. A better understanding of the exact mechanism is crucial for the development of practical applications such as emergency signs, traffic signage, dials and displays, textile printing, medical diagnostics, and more. Eu^{2+} activated long-lasting phosphors will play a vital role in the bright future of persistent luminescence.

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