Feature issue introduction: persistent and photostimulable phosphors – an established research field with clear challenges ahead

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Abstract: Persistent phosphors have the ability to emit light long after the excitation has ended, typically by using thermal energy to liberate previously trapped charges. Alternatively, also photons can be used for the detrapping, leading to optically stimulated luminescence (OSL). This particular field of phosphor research has seen a strong expansion over the past two decades, with a steady growth of the materials library, an improved structural and luminescence characterization and the development of novel applications. Despite this success, clear challenges lie ahead in terms of a deeper understanding of the trapping mechanism and an associated optimization of the energy storage capacity being crucial for many applications. This focus issue "Persistent and Photostimulable Phosphors" within *Optical Materials Express* features papers presented at the third International Workshop on Persistent and Photostimulable Phosphors (IWPPP 2015) held at the University of Texas at Arlington.

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1. Introduction

Persistent luminescence is a specific type of luminescence for which the emission is delayed beyond the normal radiative lifetime of the luminescent center. The delay can amount to minutes, hours or even days, which is exploited in emergency and safety signage, bioimaging, watch dials, toys, surveillance applications, counterfeiting and as light source for photodynamic activation to treat cancers and other diseases [1–3]. The defects, or traps, present in a persistent phosphor can store excitation energy under the form of trapped charge carriers. Apart from the possibility of tunneling recombination, temperature is the main driving force in the release of the trapped charges and the subsequent light emission, typically following recombination at the luminescence center. Photostimulable phosphors are closely related compounds, where instead of thermal energy, photons are used to release previously trapped charges. Optical stimulation as an analytical tool for persistent phosphors has gained increasing interest in the past years. Next to showing that a specific persistent phosphor is indeed sensitive to infrared light, OSL (optically stimulated luminescence) can offer great insight in the nature of the defects once spectroscopic analysis can be added to the stimulating light [4]. OSL is however more than an analytical tool for persistent phosphors. Katayama *et al*. show the

application potential in bioimaging [5] and Tydtgat *et al*. advocate a more thorough study of the effect of optical detrapping by the excitation light, simultaneously used to fill traps in persistent phosphors [6].

The subfield of luminescence research dealing with persistent phosphor – virtually inexisting twenty years ago – became firmly established in 2013, when a markedly stronger relative growth in scientific output was observed compared to 'general' luminescence [1]. This might partially be related to the specific forum which was created for researchers in this particular subfield of luminescence. After previous editions in 2011 (Ghent, Belgium [7],) and in 2013 (Guangzhou, China [8],), about 160 participants attended the 2015 International Workshop on Persistent and Photostimulable Phosphors (IWPPP 2015) in Arlington, Texas (Fig. 1).

Fig. 1. Group picture of the participants at the IWPPP 2015 workshop in Arlington, Texas. Reprinted with permission from the College of Science, the University of Texas at Arlington, www.uta.edu/3ppp

Hundreds of persistent phosphors have now been identified and reported [1, 9, 10]. Although this exploratory research is interesting from a fundamental and spectroscopic point of view, many compounds display only a limited trapping capacity – leading to a low persistent luminescence intensity and short duration – or unattractive excitation wavelengths are needed to induce charging (e.g. 254 nm), which compromises their use in many (traditional) applications.

It is obvious that research into deep red to infrared emitting persistent phosphors – specifically based on Cr^{3+} – gets firm ground [11], which is also reflected in this Feature Issue. Heterogeneous doping, e.g. a transition metal as the luminescence center and a lanthanide ion influencing the trapping (TM + Ln^{3+}), offers new routes for phosphor optimization [12, 13]. Nevertheless, trap filling in the visible remains an issue for most Cr^{3+} based persistent phosphors [14] and constitutes one of the main challenges, in addition to the difficulties to obtain the accurate particle sizing required for bioimaging applications.

2. Feature issue highlights

The current era of research in persistent phosphors started twenty years ago with the publication on the green emitting $SrAl_2O_4$:Eu,Dy by Matsuzawa *et al*. [15]. Although strontium aluminate phosphors constitute the largest fraction of the commercial production, several aspects about the trapping and detrapping processes have not yet been elucidated for this particular set of materials. This is partly related to complications caused by the presence of two emission bands, which were assigned to the two strontium sites [16, 17].

In a systematic study, Bierwagen *et al*. focussed on the luminescence intensity and lifetime of both emission bands as a function of temperature and of europium concentration in $SrAl_2O_4$:Eu [18]. Although the blue emission band quenches around room temperature, energy transfer to the green emission center rescues the overall efficiency of the phosphor. Based on the biexponential nature of the luminescence lifetime, it was concluded that different sets of europium ions exist, depending on their

interaction with defects in the material. This detailed study shows the complexity of energy transfer processes, even in the absence of the commonly added Dy^{3+} codopant.

In the case of $SrAl_2O_4$:Eu,Dy, Hagemann *et al.* recently suggested that optical detrapping by short wavelength ultraviolet radiation could also be relevant, next to the common thermally assisted detrapping [19]. This was investigated in detail by Tydtgat *et al.* on the blue emitting $Sr_2MgSi_2O_7$:Eu,Dy persistent phosphor, taking advantage of the fact that a thermal barrier exists for the charge trapping [6]. Consequently, when illuminating the phosphor at low temperature, no creation and subsequent trapping of charge carriers occurs. By illuminating a previously optically charged sample at low temperature, it could be shown however that the total number of trapped charges decreased. This behavior was simulated by a numerical model, showing that this optically stimulated luminescence at the excitation wavelength limits the overall trapping capacity of a persistent phosphor, which could have strong impact on several applications. Finally, it might also complicate the comparison of literature data for a specific compound, as the obtained trap distribution might depend on the excitation conditions, such as the excitation wavelength and the intensity.

While Eu^{2+} and Cr^{3+} are presumably the most popular dopant ions for emission in the visible and the deep red part of the optical spectrum, respectively [9–11], Jin *et al.* report on the persistent luminescence in Li_2MgGeO_4:Mn^{2+} [20]. Next to a relatively broad emission band related to the host itself, addition of Mn^{2+} leads to a green persistent luminescence. The thermoluminescence spectrum is broad, spanning from 50 to 250 °C. Unfortunately, the persistent luminescence can only be induced by UV excitation (at 254 nm).

Yu *et al.* report on the persistent luminescence in $BaZr_4(PO_4)_6$, which is characterized by a broad emission spectrum peaking at 475 nm [21]. It is found that annealing in a reducing CO atmosphere and codoping with Eu^{3+} positively influence the intensity of the persistence luminescence, with clear changes in the shape and position of the thermoluminescence glow peaks. Co-doping with Eu^{3+} only leads to a limited Eu^{3+} luminescence under steady state excitation – explained by a limited transfer from the host – but that in the persistent luminescence spectrum no trivalent europium is detected. Its main effect is the creation of additional traps.

In recent years, garnets have received considerable attention due to the presence of multiple cation sites and a broad range of compositional variations, altering for instance the band gap energy and the probability of photoionization after excitation. In this Feature Issue there are several reports on garnet compounds. Ahn and Kim investigated the upconversion luminescence in $Lu_3Al_5O_{12}$:Yb^{3+},Er^{3+} [22]. For $Lu_3Al_2Ga_3O_{12}$, a host referred binding energy scheme was constructed by Wang *et al.* for the energy levels of the divalent and trivalent lanthanides [23]. Tb^{3+} was taken as the luminescence and recombination center, while Sm^{3+}, Eu^{3+} and Yb^{3+} were determined as suitable electron traps upon co-doping. For Yb^{3+}, the deepest traps were found, yet with a broad trap depth distribution which was characterized by thermal cleaning and fading experiments. Although the intensity of the persistent luminescence at room temperature initially follows an exponential profile, tunneling recombination becomes more important in the later stages of the decay and contributes significantly to the intensity beyond one hour after the end of the excitation.

Katayama *et al.* looked at the charging of $Y_3Al_2Ga_3O_{12}$:Cr^{3+} as a function of the excitation wavelength [5]. Ultraviolet radiation (254 nm) is a straightforward way to induce the persistent luminescence. Based on the thermoluminescence glow curve, two distinct traps are found, with the deeper one hardly contributing to the persistent luminescence at room temperature. Blue light (455 nm) leads to the filling of even deeper traps, albeit with a very low efficiency, while red light cannot induce any charge trapping. It was observed that low energy photons (red to near infrared) can lead to optically stimulated detrapping, when the phosphor was first excited at short wavelength. Optical stimulation with 808 and 977 nm mainly acts on the shallower traps, while red light (625 nm) liberated trapped charges from both the shallow and deep traps. Although a fraction of these charges leads to immediate recombination at the chromium centers, a considerable fraction is retrapped at the shallower traps, leading to an increase in the afterglow emission intensity after ending the optical stimulation.

This observation offers an interesting approach for reviving the persistent luminescence after the initial decay in the case of *in vivo* bioimaging, where the typical excitation wavelength needed to refill traps is often too short to have a sufficiently long path length in tissue. The photostimulation by means of red light is much easier to achieve, while the retrapping in shallower traps – rather than immediate recombination - again leads to a decoupling between stimulation (one minute in example [5]) and detection, avoiding autofluorescence issues.

Katayama *et al.* tested several lanthanide co-dopants (Sm^{3+}, Eu^{3+} and Tm^{3+}) to enhance the deep red persistent luminescence of $LaAlO_3:Cr^{3+}$, after which samarium was selected for providing the most suitable trap depth [13]. While the charge trapping can easily be induced upon UV excitation *via* the $^4A_2$-$^4T_1$ transition of Cr^{3+} (and potentially also *via* a metal-to-metal charge transfer), longer excitation wavelengths are less efficient, leading also to the preferential filling of deeper traps. It was concluded that for excitation around 400 nm a tunneling process is responsible, without the involvement of the conduction band, for which the Cr^{3+}-Sm^{3+} proximity is required. A strong athermal tunneling detrapping process was observed. Upon co-doping with Sm^{3+}, a lower optimum Cr^{3+} doping concentration is found, suggesting that the optimization of dopant and co-dopant concentrations should not be performed independently.

Zhang *et al.* showed that a cyan persistent luminescence can be discerned in $La_3GaGe_5O_{16}$ [24]. Upon doping with Cr^{3+}, the characteristic deep red emission is observed along with an enhancement of the intensity of the persistent luminescence. The doping also induces additional traps with a different trap depth compared to the host-related defects. By creating a Ge/O deficiency of 1%, the intensity could be further increased. It remained however below the intensity for the benchmark $ZnGa_2O_4:Cr^{3+}$ persistent phosphor.

Hu *et al.* studied the impact of Si co-doping on the steady state and persistent luminescence properties of $ZnGa_2O_4:Cr^{3+}$ [25]. The influence of the Si concentration on the afterglow intensity is not very straightforward. At low concentrations it indeed enhances the density of the traps already present without co-doping, leading to an increased intensity of the persistent luminescence, while for higher concentrations deeper traps are being formed, leading to an initially lower intensity.

An interesting correlation is reported by Li *et al.* between photocatalytic activity and persistent luminescence [26]. Upon co-doping $Ga_2O_3:Cr^{3+}$ with In^{3+}, the photocatalytic activity increased, as measured by the degradation of Rhodamine B upon illumination with a mercury lamp. Simultaneously, the co-doping with In^{3+} strongly increased the persistent luminescence, due to the creation of additional and deeper traps, while leaving the steady state photoluminescence of Cr^{3+} unaffected. It was hypothesized that the photogenerated charge carriers can be maintained for a longer time – before recombination at the Cr^{3+} centers occurs – when more traps are present. Hence the trapping capacity can be correlated to the photocatalytic activity. The authors assume that temporary trapping increases the possibility for charge carriers to migrate to the surface of the particles, thereby suggesting that the thermal release of trapped charges occurs via the conduction band, assuring the mobility of charge carriers.

Given that the human eye is not very sensitive to the deep red emission of Cr^{3+}, especially not in the case of low light levels [27], these phosphors have no useful application in the area of safety and emergency signage. The research is mainly driven by the use of these Cr^{3+}-doped compounds for in vivo bioimaging, where the Cr^{3+} nicely falls in the first transparency window [14, 28]. In that respect, Mason *et al.* applied the chemiluminescence process used in glowsticks to study the wavelength dependency of the light penetration in two phantoms, based on dark and light deli meat [29]. Quantum dots with an emission at 780 nm were helpful in red-shifting the chemiluminescence emission, to enhance the light penetration. The approach can be used as model system for *in vivo* bioimaging based on persistent phosphors.

3. Future and perspectives

Using persistent phosphors for biomedical imaging – thereby avoiding autofluorescence – and photodynamic activation are emerging areas attracting strong attention. This development has clearly steered a significant share of research in this field towards a new

class of materials [2, 11, 28]. While strongly performing materials have been identified, along with crucial knowledge on their storage mechanism [30, 31], a challenge remains to prepare phosphors with an appropriate particle size for a specific application, while maintaining a large storage capacity. Furthermore, a solution to the limited *in situ* excitation with relatively long wavelength light should be pursued, although the demonstration of OSL based 'recharging' somewhat alleviates this issue [5]. For the longer term, this bioimaging approach should move from fundamental and proof-of-concept studies to a technique being regularly applied in bioimaging applications. In addition, the development of specific persistent and photostimulable phosphors for security and surveillance applications can meet certain societal demands.

Regarding the mechanisms underlying the trapping and detrapping processes, considerable efforts are still needed. Key questions are related to the chemical nature of the traps and the interaction between traps and luminescence centers. Occasionnally even the identification of the emitting centre deserves more attention, as the role of unintentially incorporated impurities should be fully recognized [32]. In addition, emphasis should be put on an absolute quantification of the energy storage capacity and the parameters which are affecting this capacity. In that respect, the fact that upon excitation also optically stimulated detrapping occurs is a phenomenon which deserves further attention.

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