

# A brief review on red to near-infrared persistent luminescence in transition-metal-activated phosphors



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## ABSTRACT

In the past few years, red to near-infrared persistent phosphors activated by transition metals ( $\text{Cr}^{3+}$  or  $\text{Mn}^{2+}$ ) received much attention. The research was triggered by a recently proposed *in vivo* imaging application and it may show more significance in the future. In this review, we try to make a full list of known  $\text{Cr}^{3+}$  or  $\text{Mn}^{2+}$ -activated compounds showing red to near-infrared persistent luminescence, which may be useful for further exploration of new compounds. We also notice that *radiance* (in units of  $\text{W sr}^{-1} \text{m}^{-2}$ ) is even more suitable than *luminance* (in units of  $\text{cd m}^{-2}$ ) to quantify the brightness of red to near-infrared persistent phosphors for the *in vivo* imaging application. Finally, we discuss the mechanism of the persistent luminescence by taking an example of  $\text{Cr}^{3+}$ -activated  $\text{Zn}_{0.98}(\text{Ga}_{1-x}\text{Al}_x)_2\text{O}_{3.98}$  persistent phosphors.

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## 1. Introduction

Persistent luminescence, generally known as phenomenon of continuous emission after the end of excitation, is also named as afterglow or long-lasting phosphorescence in the literature [1]. However, persistent luminescence is referred to a special case of thermally stimulated luminescence at a given temperature (usually at room temperature), which should be distinct from phosphorescence due to forbidden transition in the luminescence center [2]. The phenomena of persistent luminescence have been observed for more than 2000 years [3] and were recorded for the first time in a scientific work at the beginning of the 17th century [4]. In the last 30 years, great interest and extensive research on the persistent luminescence in both science community and industry field brings out a big list of excellent persistent phosphors for some glow-in-the-dark applications [5]. Till now, a lot of blue and green persistent phosphors showing long-lasting persistent luminescence have been investigated. Representative examples should go to  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$  and  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  phosphors [6,7]. The latter phosphor lasts for more than 2000 min before decaying to  $0.32 \text{ mcd m}^{-2}$ . On the other hand, the number of known red persistent phosphors is much less than those of blue and green persistent phosphors. Also, red persistent phosphors with the same brightness (strictly in physics is *luminance*, refer to Section 3.1) to the blue and green counterparts are still not available.

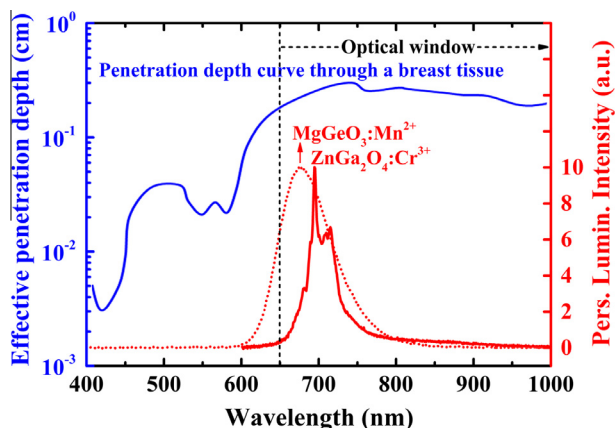
In 2007, Chermont et al. proposed a novel *in vivo* imaging method by using red to near-infrared (NIR) persistent nano-particles as an optical label, to greatly improve the signal to noise ratio in the next-generation bio-imaging technology [8]. This new application adds more importance to the development of red to NIR persistent phosphors with sufficient intensity and decay time.

Reviewing on the reported red to NIR persistent phosphors, the luminescence center can be rare earth ions ( $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$ , or  $\text{Pr}^{3+}$ ) or transition metal elements ( $\text{Cr}^{3+}$  or  $\text{Mn}^{2+}$ ). Red persistent phosphors activated by rare-earth ions, such as  $\text{CaS}:\text{Eu}^{2+}$  or  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  phosphors, were extensively investigated several years ago [9–12]. However, these hygroscopic sulphides, show a serious problem in chemical instability for the biological application. Recently, the interest on red to NIR persistent phosphors was largely shifted to transition-metal-activated oxide compounds. Especially,  $\text{Cr}^{3+}$  or  $\text{Mn}^{2+}$ -doped persistent phosphors with excellent chemical stability, suitable emission range in the optical window (from 650 to 1300 nm where optical signal shows much deeper penetration distance through biological tissues; Fig. 1) [13], and long-lasting persistent luminescence, dominate in the related reports from 2010. A brief review on the transition-metals-activated persistent phosphors may be useful to understand the new progress on this research field.

Compared with two general reviews on  $\text{Eu}^{2+}$ -doped and non- $\text{Eu}^{2+}$ -doped persistent phosphors by Smet et al. [14,15] and a review specially focused on the mechanism of persistent luminescence by Hölsä et al. [2], this review emphasize the state-of-the-art development of red to NIR persistent phosphors activated by transition metals ( $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$ ). We also make some remarks on these red

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**Fig. 1.** Effective penetration depth of light through a breast tissue (blue) [13]. Persistent luminescence spectra of  $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$  (solid) and  $\text{MgGeO}_3:\text{Mn}^{2+}$  (dot) phosphors (red). The emission is mostly located in the optical window for biological tissue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to NIR persistent phosphors, considering their main applications for *in vivo* imaging application by using electronic devices rather than direct observation by human eye.

## 2. Known compounds of red to NIR persistent phosphors activated by $\text{Cr}^{3+}$ or $\text{Mn}^{2+}$

We try to make a full list of known red to NIR persistent phosphors activated by  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$  in Tables 1 and 2, respectively. The lists show that the numbers of the known  $\text{Cr}^{3+}$  or  $\text{Mn}^{2+}$ -activated persistent phosphors are much less than those of  $\text{Eu}^{2+}$ -activated persistent phosphors [14]. Most of these papers on  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$ -activated persistent phosphors were published after 2007, the year when the new *in vivo* imaging method was proposed. The number of related papers is expected to greatly increase in the coming years.

Interestingly, all of the known  $\text{Cr}^{3+}$ -activated persistent phosphors are gallate compounds. The incorporation of  $\text{Cr}^{3+}$  luminescence center into octahedral  $\text{Ga}^{3+}(\text{VI})$  site yields emission from 650 to 1000 nm, which is suitable for the *in vivo* imaging application. More importantly, these gallate compounds contain abundant traps with suitable depth for persistent luminescence at room temperature (RT). On the other hand, many aluminate compounds with the similar crystals structure (for example,  $\text{ZnAl}_2\text{O}_4$  or  $\text{Al}_2\text{O}_3$ ) do not show persistent luminescence because of much deeper traps [38].

As a host material for  $\text{Cr}^{3+}$ -activated persistent phosphors, the  $\text{ZnGa}_2\text{O}_4$  and related solid solutions with spinel structure have been attracting the most attention. In 2011, Bessière firstly reported

persistent luminescence at around 695 nm in  $\text{Cr}^{3+}$ -doped  $\text{ZnGa}_2\text{O}_4$  crystals [16]. Pan [24] and Allix [25] greatly improved the red persistent luminescence by partially substituting Zn + Ge for Ga by to form  $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$  solid solution. According to Ref. [24], the persistent luminescence is detectable by a night vision equipment up to 360 h after the excitation source was removed. We also found that by codoping  $\text{Bi}_2\text{O}_3$  into the  $\text{ZnGa}_2\text{O}_4$  crystals, the intensity of red persistent luminescence can be improved by 10 times [19]. Abdokayum succeeded to demonstrate *in vivo* imaging experiments by using  $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4:\text{Cr}^{3+}, \text{Pr}^{3+}$  nano-particles. The feasibility, including  $\text{Cr}^{3+}$  persistent luminescence duration, particle biocompatibility, water solubility etc. was proved in this study [26]. The  $\text{ZnGa}_2\text{O}_4$  crystal and related solid solutions may be the most promising host materials in this field till now.

As shown in Table 2, the  $\text{Mn}^{2+}$ -activated compounds showing red to NIR persistent luminescence can be grouped to (i) crystals with  $\text{ABO}_3$  composition (A = alkali earth or transition metal, B = Si or Ge) and (ii) phosphate crystals. The research of the phosphate persistent phosphors is earlier than that of the  $\text{ABO}_3$  phosphors. In these crystals, incorporation of  $\text{Mn}^{2+}$  into alkali earth sites with octahedral (Octa.) coordination is indispensable to obtain emission in longer wavelength (red to NIR). On the other hand, when incorporated into a tetrahedral (Tetra.) alkali earth site, for example, in  $\text{ZnGa}_2\text{O}_4$  or  $\text{MgGa}_2\text{O}_4$  crystals (not listed in Table 2), green persistent luminescence is observed [53]. The Tanabe-Sugano diagram for  $\text{Mn}^{2+}$  ion ( $3d^5$ ) is shown in Fig. 2 [54,55]. The emission of  $\text{Mn}^{2+}$  ( ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$  transition) in tetrahedral sites is in shorter wavelength region than that in octahedral sites.

## 3. General remarks

### 3.1. Evaluation method on the red to NIR persistent luminescence intensity

One of the technical criteria for persistent phosphor is its brightness after the removal of excitation source. Among many physical quantities in optical physics (part of them are listed in Table 3), *luminance* (in units of  $\text{cd m}^{-2}$ ) is generally adopted to quantify the brightness of persistent phosphors in industrial patents or international standards. For example, according to the International Maritime Organization (IMO), persistent phosphors suitable for night-vision application should provide *luminance* at least  $15 \text{ mcd m}^{-2}$  at 10 min. and greater than  $2 \text{ mcd m}^{-2}$  at 60 min after the removal of all external excitation sources [56]. Also, the *decay time* of a persistent phosphor is generally defined as the time when the *luminance* has decayed to a certain level, typically  $0.32 \text{ mcd/m}^2$  (roughly 100 times of the low limit of human eye sensitivity in dark-adapted condition) [57].

Exactly, the *luminance* is not a pure physical quantity, but a virtue quantity which considers the sensitivity of human eye. The sensitivity of human eye depends on the wavelength of light (radiation), i.e. the same *radiant flux* (in units of W) in different

**Table 1**  
Known compounds of red to NIR persistent phosphors activated by  $\text{Cr}^{3+}$ .

Host material	Incorporated site	Emission region (nm)	Reference	Published year
$\text{ZnGa}_2\text{O}_4$	$\text{Ga}^{3+}(\text{VI})$	650–730	[16–21]	2011–2014
$\text{MgGa}_2\text{O}_4$	$\text{Ga}^{3+}(\text{VI})$	650–770	[22,23]	2013
$\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$	$\text{Ga}^{3+}(\text{VI})$	680–800	[24–27]	2012–2014
$\text{Zn}_{1.5}\text{Ga}_1\text{Sn}_{0.5}\text{O}_4$	$\text{Ga}^{3+}(\text{VI})$	680–800	[28]	2014
$\text{La}_3\text{Ga}_5\text{GeO}_{14}$	$\text{Ga}^{3+}(\text{VI})$	660–1100	[29,30]	2010
$\text{LiGa}_5\text{O}_8$	$\text{Ga}^{3+}(\text{VI})$	680–760	[31]	2013
$\text{Ga}_2\text{O}_3$	$\text{Ga}^{3+}(\text{VI})$	650–850	[32,33]	2011, 2013
$\text{SrGa}_{12}\text{O}_{19}$	$\text{Ga}^{3+}(\text{VI})$	660–900	[34]	2014
$\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{10}$	$\text{Ga}^{3+}(\text{VI})$	660–750	[35]	2014
$\text{Gd}_3\text{Ga}_5\text{O}_{10}$	$\text{Ga}^{3+}(\text{VI})$	660–800	[36,37]	1993, 2009

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