Red to near-infrared persistent luminescence in transition metal ion activated phosphors

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Red-to-near infrared persistent phosphors have attracted great attention because they are promising candidates for in vivo imaging. However, for most of the persistent phosphors that are activated only by ultraviolet (UV) light, the detection time is limited because persistent luminescence decays with time and UV excitation cannot be repeated due to the opacity of living tissues to UV radiation. Therefore, we have developed persistent phosphors with perovskite and garnet structures, which show 1) persistent luminescence at an optimum wavelength with high transparency for living tissue, 2) with brighter and longer persistent luminescence, and 3) with an additional function leading to long-term in vivo imaging capability.

Key-words: Persistent luminescence, Transition metal oxide, Luminescence

1. Introduction

Persistent phosphors are materials that show a delayed luminescence, that is, they emit light after the cessation of excitation. These materials are widely used as luminous paints in safety signs, night lighting, arts and decoration. In recent years, red to near infrared (NIR) persistent phosphors have attracted great attention as promising emitters for in vivo imaging applications.3)–5)

The delay in luminescence originates from the presence of carrier trapping defects in the forbidden bandgap of these materials. In most cases, these defects are generated during irradiation with X-ray or ultraviolet (UV) light, and in rare cases, by visible light excitation. Persistent luminescence is observed when the trap depths of these defects are sufficiently small to allow charges to be released by ambient thermal energy. In contrast, materials that have deeper traps are called storage phosphors. Here, the stored carriers are released by providing additional thermal- or photostimulation (PS) resulting, respectively, in thermally stimulated luminescence (TSL) or photo-stimulated luminescence (PSL). TSL glow curves are measured by recording TSL intensity against temperature at a constant heating rate. This is an important technique that provides information on the trap depths and their distribution in the luminescent material.

The demand for persistent luminescence at a particular wavelength depends on the corresponding application. Figure 1 shows the persistent luminescence spectra of several visible to NIR persistent phosphors,6)–12) along with luminescence curves (photopic and scotopic) and the effective penetration depth of living tissue. It is seen that the blue-green colors (shorter wavelength region in the visible light range, 400–550 nm) are suitable for luminous paints. These colors are obtained by Eu2+ -activated alkaline aluminate by changing the host lattice composition which leads to the ligand field splitting of Eu2+ 5d states. Long and bright persistent luminescence can be obtained by lanthanide co-doping. On the other hand, for in vivo imaging applications, the red-to-NIR region is suitable, since biological tissues have higher transmittance in this range of wavelength. In particular, the range from 650 to 950 nm is called the first biological window because of its compatibility with silicon photo detector imaging (see Fig. 1 lower graph).14)–15)

In vivo imaging using persistent phosphors was first demonstrated in 2007 using Mn2+-activated Mg3Bi2O5 nano particles.16) The main advantage of using red to NIR persistent phosphor for in vivo imaging when compared to other fluorescent probes is that persistent luminescence can be used without excitation light during imaging. Also, excitation before injection leads to higher signal-to-noise ratio by avoiding scattering of the excitation light, as well due to the absence of the auto-fluorescence in biological tissues.16)–17) To date, many red-to-NIR persistent phosphors activated with Mn2+ and Cr3+ ions, such as Ca2+Zn2+Mn2+Mg0.8Si2O5:Eu2+–Dy3+–Mn2+ (685 nm),16) CaMgSi2O6:Mn2+ (800 nm),18) and Sr2+Mn2+:LaAlO3 (800 nm)19) have been developed. In this paper, we introduce a material activated with Mn2+ and Cr3+ ions, as promising candidate for in vivo imaging.
(685 nm),19,19) MgGeO3: Mn2++-Bi3++ (680 nm),20) ZnGa2O4:Cr3+ (694 nm),20,21) LiGaO2:Cr3+ (716 nm),22) Cr3+-doped zinc gallgenanites (696 nm),23,24) CaGa3Ge2O12:Cr3+-Yb3+-Tm3+ (750 nm),25) La2Ge2O7:Cr3+ (785 and 1030 nm),26) LaAlO3:Cr3+-Sm3+ (734 nm), Y3(Al,Ga)5O12:Cr3+11,30) have been reported, for which the transition wavelength is within the first biological window.

However, the most critical problem in using persistent phosphor for in vivo imaging is that the detection time is limited because, persistent luminescence decays with time and the UV excitation cannot be repeated owing to the opacity of living tissues to UV. Therefore, for long-term in vivo imaging, several materials with additional characteristics, including upconversion,28) red excitable persistent luminescence,29) PSL under NIR photostimulation,30–32) and PS induced persistent luminescence33,33) have been reported.

This review describes the results on two red to NIR phosphors, namely, Cr3+-activated LaAlO3 perovskite, and Y3Al5Ga3O12 garnet, both of which show persistent luminescence in the first biological window. Both have bright and long persistent luminescence. In particular, LaAlO3:Cr3+ shows persistent luminescence at an optimum wavelength and enhancement of persistent luminescence intensity was accomplished by lanthanide co-doping. In Y3Al5Ga3O12:Cr3+, PS induced persistent luminescence, which can be used in long-term in vivo imaging, was observed.

2. Luminescence of Cr3+ in oxide lattices

Cr3+-activated phosphors show luminescence in the deep-red to NIR region due to intra-atomic 3d–3d transitions. The Cr3+ ion shows two kinds of luminescence depending on the crystal field strength of the host lattice, namely, sharp luminescence lines due to the E→A2 (R-line) transitions in a strong crystal-field host and a broad luminescence band due to the T2→A2 transition in a weak crystal-field host. The sharp R-line luminescence is due to the E excited state, which has a small dependence on ligand field strength (Dq), which is well characterized by the shape of the Tanabe–Sugano diagram for 3d3 electronic configuration in a 6-fold symmetry site24) shown in Fig. 2. The emission energy of the E→A2 transition is ∼21B in most phosphors and this emission can be observed in high efficiency when the ligand field strength Dq/B is sufficiently large; here, B is the Racah parameter and Dq is the crystal field parameter. Cr3+ in LaAlO3 is known to show one of the longest ones among the most commonly reported Cr3+-doped oxide materials.35–37) In the LaAlO3 lattice, B (663 cm−1) is relatively small and Dq/B (2.7) is larger when compared to other oxide phosphors. The E energy in Cr3+-activated phosphors can be described quantitatively, by the small values for both B and the Racah parameter C in this host.37) In Fig. 2(b), the R-line transition energies in several oxide lattices are plotted as a function of the non-dimensional quantity $\beta = \sqrt{(B/B_0)^2 + (C/C_0)^2}$ where $B_0$ (918 cm−1) and $C_0$ (4133 cm−1) represent the Racah parameters of free Cr3+ ion.39) There is a tendency that a smaller $\beta$ leads to a lower R-line energy, which explains the stronger nephelauxetic effect observed for Cr3+ in the LaAlO3 lattice when compared with other oxides.39) Although Cr3+ is known to show a longer R-line wavelength in other perovskite materials such as SrTiO3 and BaTiO3,26,60) LaAlO3 is a better host material for Cr3+ luminescent centers than the titannes because, the Al3+ ion is electronically inactive (in contrast to the Ti4+ ion) and Cr3+ is stabilized at the Al3+ site without change in valence state. In addition, LaAlO3:Cr3+ shows low quenching at ambient temperature. In the case of the Y3Al5Ga3O12 host lattice, the R-line at 690 nm as well as the $^4T_2\rightarrow^2E$ transitions can be observed at ambient temperature, because the crystal field strength is close to the cross point between the $^2T_2$ and E levels (Dq/B∼2).

3. Deep red persistent phosphor:

LaAlO3:Cr3+ perovskite

In 2015, we first reported persistent luminescence in Cr3+-activated LaAlO3 perovskite lattice, where enhanced persistent luminescence was observed by Sm co-doping.12) Cr3+-doped and Cr3+-Ln3+ (Ln = Sm, Eu, Tm)-co-doped LaAlO3 ceramics were synthesized using a solid-state reaction method and persistent luminescence properties were investigated. As discussed in section 2, Cr3+ in LaAlO3 shows a relatively longer R-line luminescence at 734 nm, which is the appropriate wavelength for in vivo imaging applications while using the first biological window. Figure 3 shows the photoluminescence (PL) excitation, PL, and persistent luminescence spectra of LaAlO3:Cr3+ as well as the TSL excitation (TSLE) spectrum of LaAlO3:Cr3+-Sm3+. To obtain TSL spectrum, TSL glow curves were measured after different wavelength excitation. Then the integrated TSL intensities were plotted as a function of excitation wavelength. The PL and persistent luminescence spectra show the same structure consisting of an R-line peaking at 734 nm, phonon side bands, and a Cr3+-Cr3+ pair luminescence line at 749 nm.41,42)

This result suggests that the PL and persistent luminescence originate from the same emitting center. The PLE shows three bands in the range 200–700 nm. These bands are attributed to $^2A_2\rightarrow^4T_2$ (522 nm), $^4A_2\rightarrow^4T_2(F)$ (426 nm), and $^4A_2\rightarrow^4T_1(P)$ (265 nm). On the other hand, the TSLE spectrum shows a band in the UV region corresponding to the $^4A_2\rightarrow^4T_1(P)$ transition. This suggests that persistent luminescence of LaAlO3:Cr3+ can be activated by UV light. However, the persistent luminescence intensity is weak for Cr3+ singly doped LaAlO3 when compared...
to ZnGa$_2$O$_4$:Cr$^{3+}$, which is one of the potential candidates to be used as a persistent phosphor in in vivo imaging.

To increase the intensity of persistent luminescence, several methods including modification of composition, reduction sintering, and introduction of an additional dopant are often adopted, which have the aim to introduce appropriate traps. Among these strategies, we have selected co-doping of lanthanide ions, and also, there are many reports in the literature, where the persistent luminescence intensity was increased by co-doping.$^{6,7,43}$ In addition, it has been revealed that the depth of the trap generated by lanthanide co-doping is closely related to the energy gap between the ground state of the divalent lanthanide ions and the bottom of the conduction band of the host. On the basis of the location of the energy levels of divalent lanthanide ions in the LaAlO$_3$ host material, as described using the zigzag curve in the Dorenbos model,$^{44}$ Sm is considered to be a candidate element for the generation of electron traps of appropriate depths.

**Figure 4** shows the persistent luminescence decay curves of LaAlO$_3$:Cr$^{3+}$, LaAlO$_3$:Cr$^{3+}$–Sm$^{3+}$, and ZnGa$_2$O$_4$:Cr$^{3+}$ recorded after the samples were excited by the xenon lamp for 5 min. The radiance (a measure of radiation flux emitted by a surface per unit solid angle per unit area) intensities of the LaAlO$_3$:Cr$^{3+}$, LaAlO$_3$:Cr$^{3+}$–Sm$^{3+}$, and ZnGa$_2$O$_4$:Cr$^{3+}$ samples 60 min after ceasing UV excitation were, respectively, $4.4 \times 10^{-4}$, $1.5 \times 10^{-2}$ and $1.6 \times 10^{-2}$ mW sr$^{-1}$ m$^{-2}$. By Sm co-doping, the radiance intensity was increased by more than 35-fold. The radiance intensity of the LaAlO$_3$:Cr$^{3+}$–Sm$^{3+}$ sample was comparable to that of the ZnGa$_2$O$_4$:Cr$^{3+}$ phosphor. On the other hand, the persistent luminescence intensity of the Tm$^{3+}$ and Eu$^{3+}$ co-doped material was $\sim 10^{-3}$ mW Sr$^{-1}$ m$^{-2}$ (not shown in Fig. 4), which is the same order of magnitude as that in the LaAlO$_3$:Cr$^{3+}$.

In order to examine the trap distribution in the materials, TSL glow curves were recorded with a heating rate of 10 K/min following excitation by a xenon lamp for 5 min. **Figure 5(a)** shows the TSL glow curves of LaAlO$_3$:0.5%Cr$^{3+}$ and LaAlO$_3$:0.5%Cr$^{3+}$–0.05%Ln$^{3+}$ (Ln = Sm, Eu, Tm) obtained by monitoring deep-red Cr$^{3+}$ luminescence (TSL glow curves of LaAlO$_3$:Cr$^{3+}$ and LaAlO$_3$:Cr$^{3+}$–Sm$^{3+}$ are from Katayama et al.$^{12}$) and (b) VRBE energy diagram for Cr$^{3+}$ and the three lanthanide divalent ions. The VRBE values of band edges and ground state divalent lanthanide ions are from Dorenbos.$^{46}$ Ex represents the excitonic level, which is 0.3 eV below the bottom of the conduction band according to the VRBE model.$^{45}$
curve peak due to Sm$^{3+}$ co-doping appears at a higher temperature than that due to Tm$^{3+}$ co-doping. If the traps created by lanthanide co-doping have similar frequency factors, for instance $s=1.0 \times 10^{13}$ s$^{-1}$, which is the same order of magnitude as the frequency factor of LaAlO$_3$ perovskite at ambient temperature, the trap depth $E_{\text{trap}}$(Sm) is 0.91 eV for Sm$^{3+}$ and 0.69 eV for the Tm$^{3+}$ co-doped sample. $E_{\text{trap}}$(Sm) is deeper than $E_{\text{trap}}$(Tm). In other words, $E_{\text{trap}}$(Sm) > $E_{\text{trap}}$(Tm). These trends can be explained by the valence reer binding energy (VRBE) model if the electron trap level is considered as Ln$^{3+} + e^{+}$ or Ln$^{3+}$[4, 44]. By referring to the VRBE diagram of LaAlO$_3$, the energy gaps (E$_{\text{e}}$(LaAlO$_3$)-CB) between the ground state of Ln$^{3+}$ ions and the bottom of conduction band is found to be 0.75 eV for Tm, 1.22 eV for Sm, and 2.47 eV for Eu; these values are at low temperature (~10 K) [Fig. 5(b)]. The observed trend in the value of E$_{\text{e}}$(LaAlO$_3$)-CB between Sm and Tm is in accordance with that of the trap depths obtained from TSL results [E$_{\text{trap}}$(Sm) > $E_{\text{trap}}$(Tm)]. Taking into account the shifting of the conduction band energy with temperature, the value of E$_{\text{e}}$(LaAlO$_3$)-CB at 300 K is quite similar to $E_{\text{trap}}$(LaAlO$_3$) estimated from the TSL peak temperature. For the Eu$^{3+}$-co-doped sample, the TSL peak temperature is estimated to be ~800 K from E$_{\text{e}}$(LaAlO$_3$)-CB in the VRBE diagram. Hence, the corresponding TSL peak is not observed in the TSL glow curve up to 450 K. From these results, it is suggested that the persistent luminescence in LaAlO$_3$:Cr$^{3+}$-Sm$^{3+}$ is caused by electron trapping and de-trapping to and from Sm$^{3+}$-related defects.

4. Photostimulation induced persistent luminescence in Y$_3$Al$_2$Ga$_3$O$_{12}$:Cr$^{3+}$ garnet

Cr$^{3+}$-activated Y$_3$Al$_2$Ga$_3$O$_{12}$ garnet (YAGG:Cr$^{3+}$) persistent phosphor has also been reported in our group[11] as a promising candidate material for in vivo imaging application. Following UV excitation, YAGG:Cr$^{3+}$ shows strong persistent luminescence peaked at 690 nm due to R-line and $\mathrm{T}_{2g}^\rightarrow$A$_2$ transitions. The persistent luminescence intensity 60 min after UV excitation is $6.7 \times 10^{-12}$ mW cm$^{-2}$ s$^{-1}$, which is stronger than those of the well-studied red-NIR persistent phosphors, ZnGa$_2$O$_4$:Cr$^{3+}$ and LaAlO$_3$:Cr$^{3+}$-Sm$^{3+}$. However, similar to LaAlO$_3$:Cr$^{3+}$-Sm$^{3+}$, persistent luminescence in YAGG:Cr$^{3+}$ can be activated only by UV excitation. In other words, this material is not a red excitable persistent phosphor like ZnGa$_2$O$_4$:Cr$^{3+}$. YAGG:Cr$^{3+}$ is both a persistent phosphor and a photo-storage phosphor because it shows two strong TSL glow peaks at ~300 K [Peak(I)] and ~400 K [Peak(II)]. The TSL peak at 400 K is stable at ambient temperature, whereas the peak at 300 K is active for persistent luminescence. Thus, deeper traps in YAGG:Cr$^{3+}$ can also be utilized for additional detection for in vivo imaging application. Taking advantage of the unique features of YAGG:Cr$^{3+}$, the effects of PS on the TSL glow curves of YAGG:Cr$^{3+}$ were studied. In this section, PS-induced persistent luminescence following red light PS in YAGG:Cr$^{3+}$ is described; this persistent luminescence can be used for repeatable in vivo imaging.

Figure 6 shows that there are two kinds of TSL glow curves. The first kind are TSL glow curves excited for 5 min by UV light followed by a waiting period of 1 h at 300 and 10 K. The second is the dependence of the PS photon energy on the TSL glow curve after de-trapping the shallower traps (I) at ambient temperature for 1 h. After 254 nm excitation for 5 min at 300 K, sample temperature was kept at 300 K for 2 h to remove the shallower trap (I). Next, the sample was either cooled down to 120 K and kept for 1 h at this temperature or subjected to PS before heating. The normal TSL glow curve after UV excitation at low temperature shows two peaks at 311 and 394 K. The corresponding trap depths $E_{\text{trap}}$, which are estimated by using the initial rise method, are 0.38 and 0.76 eV, respectively. These values represent the shallowest trap depth for each of these particular type of trap/ TSL peaks. Therefore, traps corresponding to the peak at 394 K are indeed deeper than those corresponding to the peak at 311 K. Only deeper traps remain 2 h after excitation at 300 K. To investigate the PS effects on TSL glow curves, these were measured to evaluate the photo-transfer phenomenon. Photo-transfer involves an electron trapped at a deep trap, which is photo-ionized and re-trapped at a shallower trap, which in turn is the key trap involved in persistent luminescence. With increasing PS energy from 1.27 to 1.98 eV, it was seen that the TSL intensity in one part of Peak (I) at ~330 K increased and peak (II) shifted to higher temperatures. This tendency was more pronounced when higher photon energy PS was used. This result strongly indicates that persistent luminescence can be re-activated by PS in the red (1.53 and 1.98 eV photons). The depth of the shallowest trap induced by the PS was estimated by applying the initial rise method to the TSL curves. The estimated trap depths for different PS energies were, 0.51 eV for 977 nm, 0.48 eV for 808 nm and 0.42 eV for 625 nm. Figure 7 shows the schemes of the mechanism of persistent luminescence, PSL and PS-induced persistent luminescence mechanisms in the YAGG:Cr$^{3+}$ based on the electron-trapping model. The energy scale is estimated from previous work.[11, 47] In Fig. 7(a), an efficient electron trapping at both traps (I) and (II) (denoted as dotted arrows) occurs through the conduction band under UV excitation at 254 nm which is illustrated by a violet arrow from the ground state of Cr$^{3+}$ to the bottom of the conduction band. After switching off the UV excitation, persistent luminescence appears mainly due to the emptying of traps (I) [denoted as dotted arrow in Fig. 7(b)] followed by recombination occurring through the conduction band [Fig. 7(b)]. After several hours, no more electrons remain trapped at the shallower traps (I) whereas electrons at the deeper traps remain trapped [Fig. 7(c)]. At this point, for example, upon 625 nm red PS [Red arrow in Fig. 7(d)], electrons are released from deep traps (II) and result in PSL. Simultaneously, partial re-trapping occurs from trap (II) to trap (I) [Fig. 7(d)]. After stopping PS, persistent luminescence is observed again as shown in Figs. 7(e) and 8.

5. Summary

Results on Cr$^{3+}$-activated red-to-NIR persistent phosphors, LaAlO$_3$:Cr$^{3+}$ perovskite and Y$_3$Al$_2$Ga$_3$O$_{12}$:Cr$^{3+}$ garnet, which
are promising candidates for in vivo imaging application, were presented in this review. Persistent luminescence at 734 nm, which is an appropriate wavelength for the first biological window, was obtained in LaAlO$_3$:Cr$^{3+}$. Sm was found to be an efficient co-dopant to increase the persistent luminescence intensity. Persistent luminescence process of lanthanide codoped perovskites was explained by an electron-trapping model. In the case of Y$_3$Al$_2$Ga$_3$O$_{12}$:Cr$^{3+}$ persistent phosphor, photo-transfer phenomenon and PS induced persistent luminescence were observed by red PS, which can be used for repeatable in vivo imaging.

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Fig. 7. Schematic of persistent luminescence, photostimulated luminescence and photostimulation induced persistent luminescence in YAG:Cr$^{3+}$. The energy level diagram corresponds to Cr$^{3+}$ states before releasing an electron and after capturing an electron (B, C, D, E). The red arrow in D denotes 625 nm PS.33)

Fig. 8. Persistent luminescence after 5 min of UV excitation followed by photostimulated persistent luminescence after 1 min red photostimulation.33)

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