A Pr$^{3+}$ doping strategy for simultaneously optimizing the size and near infrared persistent luminescence of ZGGO:Cr$^{3+}$ nanoparticles for potential bio-imaging

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A Pr³⁺ doping strategy for simultaneously optimizing the size and near infrared persistent luminescence of ZGGO:Cr³⁺ nanoparticles for potential bio-imaging.

The microstructure and optical properties of spinel-phase Zn₂Ga₂.⁹₈ₓGe₀.₇₅O₈:Cr₀.₀₂₀Prₓ near infrared persistent luminescence nanoparticles are reported. Pr³⁺ doping leads to the appearance of more anti-site pairs (Ga°₂ₙ – Zn°₂ₙ) around distorted octahedral Cr³⁺ ions and the enhanced 697 nm emissions of the interior and surface Cr³⁺ ions in the nanoparticles.

As featured in:

A Pr\(^{3+}\) doping strategy for simultaneously optimizing the size and near infrared persistent luminescence of ZGGO:Cr\(^{3+}\) nanoparticles for potential bio-imaging

Zheng Gong,\(^a\) Yuxue Liu,\(^b\) * Jian Yang,\(^a\) Duanting Yan,\(^a\) Hancheng Zhu,\(^a\) Chunguang Liu,\(^a\) Changshan Xu\(^a\) and Hong Zhang\(^a\) *

Spinel-phase \(\text{Zn}_2\text{Ga}_{2.98-x}\text{Ge}_{0.02}\text{O}_8\cdot\text{Cr}_{0.02}\cdot\text{Pr}_x\) (ZGGO:Cr\(^{3+}\),Pr\(^{3+}\)) near infrared (NIR) persistent luminescence nanoparticles (PLNPs) with different amounts of Pr\(^{3+}\) dopant were prepared by a hydrothermal method in combination with a subsequent annealing in a vacuum. For these nanoparticles, the averaged particle size decreases from 64 to 37 nm with increasing Pr\(^{3+}\) doping concentration from 0 to 0.025 and Cr\(^{3+}\) and Pr\(^{3+}\) ions are uniformly doped into the interior and surface of a single nanoparticle. It can be found that Pr\(^{3+}\) doping leads to the appearance of more anti-site pairs (\(\text{Ga}_{\text{Zn}}-\text{Zn}_{\text{Ga}}\)) around distorted octahedral Cr\(^{3+}\) ions and enhanced NIR emissions around 697 nm, which originate from the \(2\text{E}(\text{F}) \rightarrow 4\text{A}_2(\text{F})\) and \(4\text{T}_2(\text{F}) \rightarrow 4\text{A}_2(\text{F})\) transitions of the interior and surface Cr\(^{3+}\) ions in the nanoparticles. In particular, for the interior Cr\(^{3+}\) ions in the Pr\(^{3+}\) doped nanoparticles, the enhanced NIR luminescence can be attributed to the suppressed energy transfer of the excited electrons from the \(4\text{T}_2(\text{F})\) level to the trap level related to anti-site pairs (\(\text{Ga}_{\text{Zn}}-\text{Zn}_{\text{Ga}}\)) around the distorted octahedral Cr\(^{3+}\) ions. Our results suggest that Pr\(^{3+}\) doped ZGGO:Cr\(^{3+}\) PLNPs have potential applications for bio-imaging.

Due to the absence of excitation during bio-imaging, the afterglow time of persistent nanomaterials is of vital importance for biomedical applications, e.g. in vivo imaging. It was luckily found that lanthanide ion doping was effective in this aspect. Li \textit{et al.} prepared rare earth ion double-doped ZGGO: Cr\(^{3+}\),Yb\(^{3+}\),Er\(^{3+}\) NIR PLNPs exhibiting a super-long afterglow time (>20 days), low toxicity and excellent biocompatibility.\(^1\) To achieve \textit{in vivo} computed tomography and NIR luminescence bio-imaging, Lu \textit{et al.} designed a ZGGO:Cr\(^{3+}\),Pr\(^{3+}\)@TaO\(_2@SiO_2\) nanoplatform.\(^4\) Abdukayum \textit{et al.} also found that NIR Cr\(^{3+}\)/Pr\(^{3+}\) codoped ZGGO PLNPs could be applied for \textit{in vivo} targeted tumor imaging.\(^2\)

Despite the advancement of chromium and lanthanide ion codoped ZGGO nanoparticles, the nature of the lanthanide doping strategy is not unravelled, especially key questions like how lanthanide doping in ZGGO:Cr\(^{3+}\) PLNPs affects the particle sizes, the trap depths and the surface and interior distributions of luminescent centers. Distinct answers of the key questions are obviously essential for smart design and optimization of ZGGO-based PLNPs for biomedical applications.

Furthermore, for transition metal ion doped oxide-based persistent luminescence materials, like CaMgSi\(_2\)O\(_4\):Eu\(^{2+}\),Mn\(^{2+}\),Pr\(^{3+}\), YPO\(_4\):Pr\(^{3+}\),Ln\(^{3+}\) (Ln = Nd, Er, Ho, Dy) and ZGGO:Cr\(^{3+}\),Pr\(^{3+}\),...
praseodymium doping plays a key role in enhancing their persistent luminescence.\textsuperscript{7,9,12} Thus, spinel-phase ZGGO:Cr\textsuperscript{3+},Pr\textsuperscript{3+} NIR PLNPs were taken as the target nanomaterial to comprehend how the lanthanide doping strategy works in controlling the particle size and enhancing the persistent luminescence. Here, the composition of the ZGGO:Cr\textsuperscript{3+},Pr\textsuperscript{3+} samples with different concentrations can be represented as Zn\textsubscript{2}Ga\textsubscript{4−x−y−z}Ge\textsubscript{y}O\textsubscript{8−z}Cr\textsubscript{x}Pr\textsubscript{y}, where x, y, and z are variables. The x values are in the range of 0−0.025. According to our previous study, the y and z values are fixed at 0.020 and 0.75, respectively.\textsuperscript{11}

For these nanoparticles, our study indicates that the enhanced NIR persistent luminescence (around 697 nm) induced by Pr\textsuperscript{3+} doping is attributed to the increased interior and surface Cr\textsuperscript{3+} in the distorted octahedral sites and the suppressed energy transfer of the excited electrons from the 4T\textsubscript{2}(4F) level to the trap levels related to anti-site pairs [Ga\textsubscript{Zn} \rightarrow Zn\textsubscript{Ga}] around distorted octahedral Cr\textsuperscript{3+} ions. In particular, the average particle size was found to be dependent on Pr\textsuperscript{3+} doping concentration and tuned from 64 to 37 nm when the Pr\textsuperscript{3+} doping concentration varied from 0 to 0.025. The improved NIR persistent luminescence of the nanoparticles achieved by adopting the doping strategy facilitates deep tissue bio-imaging.

### Experimental

Zn\textsubscript{1},Ga\textsubscript{2−x−y−z}Ge\textsubscript{y}O\textsubscript{8−z}:Cr\textsubscript{x}Pr\textsubscript{y} nanoparticles with different amounts of Pr\textsuperscript{3+} (x = 0, 0.005, 0.010, 0.015, 0.020, 0.025) were synthesized by a hydrothermal method in combination with a subsequent heat treatment. A mixture of zinc acetate (99.99\%) (Aladdin), gallium(m) nitrate hydrate (99.9\%) (Sigma-Aldrich), germanium(m) chloride (99.99\%) (Sigma-Aldrich), chromium(m) nitrate nonahydrate (99.95\%) (Aladdin), and praseodymium oxide, were not detected, indicating the pure phase spinel structure of the ZGGO:Cr\textsubscript{0.020},Pr\textsubscript{x} samples. Since the radii of Cr\textsuperscript{3+} (0.62 Å) and Ge\textsuperscript{4+} (0.54 Å) ions are similar to the Ga\textsuperscript{3+} (0.62 Å) ionic radius, we believe that the Cr\textsuperscript{3+} and Ge\textsuperscript{4+} ions might substitute for Ga\textsuperscript{3+} ions located at octahedral sites in the ZnGa\textsubscript{2}O\textsubscript{4} spinel structure. This is supported by the study reported by Allix et al., who believed that different substitution elements, such as Cr\textsuperscript{3+}, Ge\textsuperscript{4+}, and Sn\textsuperscript{4+}, almost occupied the octahedral sites in ZnGa\textsubscript{2}O\textsubscript{4} materials.\textsuperscript{6} Although Pr\textsuperscript{3+} (0.99 Å) is much larger in radius than Ga\textsuperscript{3+} (0.62 Å), it is likely that Pr\textsuperscript{3+} ions tend to replace Ga\textsuperscript{3+} ions at the octahedral sites in ZGGO:Cr\textsubscript{0.020},Pr\textsubscript{x} powders.\textsuperscript{6,11,13,14}

To determine the grain size of the powders, TEM images of ZGGO:Cr\textsubscript{0.020},Pr\textsubscript{x} powders with different amounts of Pr\textsuperscript{3+} were obtained and are shown in Fig. 2a–f. Table 1 gives the average grain size and size distribution of the corresponding samples. For the undoped sample (x = 0), the particles with a cubic shape

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**Fig. 1** The XRD patterns of ZGGO:Cr\textsubscript{0.020},Pr\textsubscript{x} nanoparticles with different Pr\textsuperscript{3+} doping concentrations (x = 0, 0.005, 0.010, 0.015, 0.020, 0.025).
The strong influence of Gd$^{3+}$ ions on the nanocrystal growth rate via surface charge modification. Thus, in our study, the decreased size of the ZGGO:Cr$^{3+}$,Pr$^{3+}$ nanoparticles might be linked to the substitution of Ga$^{3+}$ by Pr$^{3+}$. Pr$^{3+}$ doping would alter the surface charge distribution of nanoparticles, suppress the diffusion of the host ions to the surface and reduce the growth rate. Therefore the size of the ZGGO:Cr$^{3+}$,Pr$^{3+}$ nanoparticles can be controlled by adjusting Pr$^{3+}$ doping concentrations.

To confirm the composition of the nanoparticles, the elemental mapping and the EDS data of the ZGGO:Cr$_{0.020}$Pr$_{0.020}$ sample were obtained and are shown in Fig. 2g–m. For a marked nanoparticle as shown in Fig. 2e, it can be seen that Zn, Ga, O and Ge elements exhibit uniform distributions throughout the whole nanoparticle. For the dopants, such as Cr and Pr elements, the uniform distributions throughout the whole nanoparticle can also be observed. This infers that Cr$^{3+}$ and Pr$^{3+}$ ions are uniformly doped in the interior and surface of the marked nanoparticle. In Fig. 2m the appearance of the strong peaks related to Zn, Ga, Ge and O elements in EDS spectra suggests the formation of the ZGGO host. The peaks related to C and Cu elements originate from the sample holder made of copper mesh grids coated with carbon. In particular, in the inset of Fig. 2m, the dopants (Cr$^{3+}$ and Pr$^{3+}$) were also clearly observed.

To reveal the effect of Pr$^{3+}$ doping on the surface distributions of Ga$^{3+}$ and Zn$^{2+}$ sites, XPS spectra of Ga 2p$_{3/2}$ and Zn 2p$_{3/2}$ core levels for the ZGGO:Cr$_{0.020}$Pr$_{x}$ nanoparticles with different amounts of Pr$^{3+}$ ($x = 0, 0.010, 0.020, 0.025$) were obtained and are shown in Fig. 3a and b. These XPS spectra were calibrated using the C 1s peak at 284.6 eV. For each of the samples with different Pr$^{3+}$ doping concentrations, not only a broad peak around 1117 eV, which is assigned to Ga 2p$_{3/2}$, appears in the binding energy range of 1114–1122 eV, but also another broad peak around 1021 eV, which is attributed to Zn 2p$_{3/2}$, can be observed in the binding energy range of 1018.5–1123.5 eV. For the undoped sample ($x = 0$), the binding energies of the Ga 2p$_{3/2}$ and Zn 2p$_{3/2}$ core levels are 1117.9 and 1021.1 eV, respectively, by fitting each of their XPS spectra using a single Gaussian function. On the basis of reported studies, it was believed that Ga$^{3+}$ (B site) and Zn$^{2+}$ (A site) ions in the ZGGO host with an AB$_2$O$_4$ spinel structure would occupy octahedral and tetrahedral sites, respectively, as shown in Fig. 3c.$^{6,16}$ Thus, it is reasonable to suggest that there exist Ga$^{3+}$ ions in the octahedral sites and Zn$^{2+}$ ions in the tetrahedral sites on the surface of the ZGGO:Cr$_{0.020}$Pr$_{x}$ nanoparticles. For the undoped sample ($x = 0$), a certain amount of Ge$^{4+}$ ($y = 0.75$) will lead to the formation of Ga vacancies ($\sim 6.25\%$). In general, the appearance of more Ga vacancies might facilitate the formation of more Zn$_{Ga}$ anti-defects.$^{17}$ However, no additional peak related to Zn ions in the octahedral sites can be found from XPS spectra, indicating that the occupancy of Ge probably does not promote the formation of more Zn$_{Ga}$ and Ga$_{Zn}$ anti-defects (Zn$^{2+}$ ions in the octahedral sites and Ga$^{3+}$ ions in the tetrahedral sites) on the surface of the undoped sample. For each of the Pr$^{3+}$ doped samples ($x = 0.010, 0.020, 0.025$), the XPS spectra of the Ga 2p$_{3/2}$ and Zn 2p$_{3/2}$ core levels are asymmetric and can be well fitted by a bi-Gaussian function. The fitted binding energies of the Ga 2p$_{3/2}$ and Zn 2p$_{3/2}$

and an average particle size of $\sim 64$ nm exhibit an aggregated behavior. For the Pr$^{3+}$ doped samples ($x = 0.005, 0.010, 0.015, 0.020, 0.025$), the particles become smaller and the size distributions become narrower. Strikingly, the averaged particle size can be controlled from 46 to 37 nm by Pr$^{3+}$ doping. Our observation is consistent with the study reported by Wang et al., who believed that the decreased size of Gd$^{3+}$ doped NaYF$_4$:Yb/Er nanoparticles relative to the undoped sample was ascribed to

Table 1 The fitting data related to the size distribution of ZGGO:Cr$_{0.020}$Pr$_{x}$ nanoparticles with different Pr$^{3+}$ doping concentrations ($x = 0, 0.005, 0.010, 0.015, 0.020, 0.025$)

<table>
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<tr>
<th>Sample</th>
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<th>Standard deviation/nm</th>
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<tr>
<td>$x = 0$</td>
<td>64</td>
<td>20</td>
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<tr>
<td>$x = 0.005$</td>
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<td>15</td>
</tr>
<tr>
<td>$x = 0.010$</td>
<td>44</td>
<td>16</td>
</tr>
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<td>$x = 0.015$</td>
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<td>$x = 0.020$</td>
<td>40</td>
<td>13</td>
</tr>
<tr>
<td>$x = 0.025$</td>
<td>37</td>
<td>13</td>
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</tbody>
</table>
core levels for the ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles with different Pr$^{3+}$ concentrations ($x = 0, 0.010, 0.020, 0.025$) are given in Table 2. After Pr$^{3+}$ doping, it can be found that a new Ga 2p$_{3/2}$ peak at a lower binding energy and a new Zn 2p$_{3/2}$ peak at a higher binding energy appear relative to the undoped sample. Usually, for Ga and Zn ions in the tetrahedral sites, their binding energies are smaller than those in the octahedral sites.\(^{17}\) It can be deduced that there are Ga and Zn ions in both tetrahedral and octahedral sites on the surface of the Pr$^{3+}$ doped samples. This result is in agreement with that reported by Bessière et al., who believed that, for zinc gallate based materials with a spinel structure, octahedral Zn and tetrahedral Ga sites appear because of the formation of anti-defects such as $\text{Zn}^{0}\text{Ga}$ and $\text{Ga}_{\text{Zn}}$.\(^{13}\) Thus, the appearance of more $\text{Zn}^{0}\text{Ga}$ and $\text{Ga}_{\text{Zn}}$ anti-defects in ZGGO might be attributed to Pr$^{3+}$ doping. In addition, for the sample with $x = 0.025$, the binding energies of the octahedral and tetrahedral Ga 2p$_{3/2}$ core levels are higher than those of the other samples. This phenomenon might be related to the deformation of the octahedra or tetrahedra, which consist of a central Ga$^{3+}$ ion and six or four oxygen anions. Therefore Pr$^{3+}$ doping could lead to the generation of distorted octahedra and tetrahedra in the ZGO host.

To further unravel the effect of Pr$^{3+}$ doping on the microstructure of the nanoparticles, Raman spectra of the ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles with different amounts of Pr$^{3+}$ ($x = 0, 0.010, 0.020, 0.025$) were obtained and are shown in Fig. 4. For the undoped sample ($x = 0$), it can be seen that Raman peaks appear at 722, 630 and 612 cm$^{-1}$. On the basis of group theory, the phonon modes related to the materials with a spinel structure at the $\Gamma$ point can be expressed as $\Gamma = A_{1g} + E_g + T_{1g} + 3T_{2g} + 2A_{2u} + 2E_u + 5T_{1u} + 2T_{2u}$.\(^{18}\) According to the study reported by Gorkom et al., $A_{1g}$, $E_g$, and $T_{2g}$ are three Raman-active modes ($k = 0$), which are at about 722, 630 and 612 cm$^{-1}$, respectively.\(^{19}\) The appearance of these Raman modes indicates the existence of a large number of ZnO$_4$ groups with symmetric stretching vibrations in the undoped sample ($x = 0$). Thus, it is possible to detect the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak$_a$ BE (eV)</th>
<th>Peak$_b$ BE (eV)</th>
<th>Peak$_a$ BE (eV)</th>
<th>Peak$_b$ BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>1021.1</td>
<td>—</td>
<td>1117.9</td>
<td>—</td>
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<td>$x = 0.025$</td>
<td>1021.0</td>
<td>1021.4</td>
<td>1117.4</td>
<td>1119.2</td>
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</table>

The samples are ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles with different Pr$^{3+}$ doping concentrations ($x = 0, 0.010, 0.020, 0.025$). $^a$ Peak$_a$ refers to the Zn 2p$_{3/2}$ or Ga 2p$_{3/2}$ peak, which corresponds to Zn$^{2+}$ or Ga$^{3+}$ in a tetrahedral site. $^b$ Peak$_b$ refers to the Zn 2p$_{3/2}$ or Ga 2p$_{3/2}$ peak, which corresponds to Zn$^{2+}$ or Ga$^{3+}$ in an octahedral site. BE represents binding energy.

The appearance of these Raman modes indicates the existence of a large number of ZnO$_4$ groups with symmetric stretching vibrations in the undoped sample ($x = 0$). Thus, it is possible to detect the
existence of tetrahedral Zn sites, which is in good agreement with the XPS analysis. For the Pr$^{3+}$ doped samples ($x = 0.010, 0.020, 0.025$), it can be found that the intensities of the Raman peaks at 722 cm$^{-1}$ dramatically decrease and the Raman peaks at 630 and 612 cm$^{-1}$ disappear. These results indicate that a number of ZnO$_4$ groups with symmetric stretching vibrations are annihilated due to Pr$^{3+}$ doping. It can be deduced that the annihilated ZnO$_4$ groups might be transformed into distorted ZnO$_4$ groups or GaO$_4$ groups related to anti-defects, such as Ga$_2$O$_3$, after Pr$^{3+}$ doping. In particular, Basavaraju et al. found that magnesium doping can lead to the promoted generation of anti-defects in the spinel material. Therefore, it can be deduced that there exist more Ga and Zn species in both octahedral and tetrahedral sites in the Pr$^{3+}$ doped ZGGO host.

In other words, Pr$^{3+}$ doping can give rise to more Ga$^{3+}$ ions occupying the tetrahedral sites and Zn$^{2+}$ ions occupying the octahedral sites in the ZGGO material.

To understand the effect of Pr$^{3+}$ doping on the luminescence properties of the nanoparticles, emission ($\lambda_{em} = 590$ nm) and excitation ($\lambda_{em} = 697$ nm) spectra of ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles with different amounts of Pr$^{3+}$ ($x = 0, 0.010, 0.020, 0.025$) were obtained and are shown in Fig. 5a and b. Upon 590 nm excitation, all the samples exhibit a superposition of a narrow NIR emission at 697 nm and a broadband NIR emission around 712 nm, which are assigned to the $^4E(^2G) \rightarrow ^4A_g(^2F)$ and $^4T_2(^4F) \rightarrow ^4A_g(^2F)$ transitions of Cr$^{3+}$ ions in the distorted octahedral site, respectively. The observed strong NIR emissions suggest that there exist distorted octahedral Ga sites in the Pr$^{3+}$ doped ZGGO host, consistent with the XPS and Raman analyses. Furthermore, it is found that the NIR emission intensity shows an initial increase and a subsequent decrease with increasing Pr$^{3+}$ doping concentration from 0 to 0.025. When $x = 0.020$, a maximum can be reached. Based on the TEM observations, the particle size decreases with increasing Pr$^{3+}$ doping concentration and this will lead to the quenched NIR emission of Cr$^{3+}$ ions. Thus, the enhanced NIR luminescence cannot be attributed to the change in particle size and maybe originates from the change in the surroundings around the luminescent center, Cr$^{3+}$, induced by Pr$^{3+}$ doping.

In Fig. 5b, each of the excitation spectra monitored at 697 nm exhibits a combination of several broad peaks in the 220–680 nm region. According to the Tanabe–Sugano diagram representing the octahedrally coordinated 3d$^3$ ion system as shown in the inset in Fig. 5b, the excitation peak around 260 nm originates from the contributions of the ZGO host and O–Ga charge transfer absorptions. Meanwhile, excitation peaks around 320, 440 and 590 nm are ascribed to the $^4A_g(^2F) \rightarrow ^4T_2(^4F)$, $^4A_g(^2F) \rightarrow ^4T_2(^4F)$ and $^4A_g(^2F) \rightarrow ^4T_1(^4F)$ transitions of Cr$^{3+}$, respectively. In particular, the appearance of the mixed 697 and 712 nm NIR emissions of the NIR ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles suggests that the luminescent center (Cr$^{3+}$ ion) locates in a site with the intermediate field, i.e. the crossing point of the $^4T_2(^4F)$ and $^4E(^2G)$ levels.

To unravel how Pr$^{3+}$ doping influences the surroundings of Cr$^{3+}$ ions, luminescence decays of the 697 nm emission of ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles with different amounts of Pr$^{3+}$ are recorded (Fig. 6). On the basis of our previous study, the NIR luminescence originates from the surface and interior Cr$^{3+}$ ions in the ZGGO nanoparticles. Therefore, all the decay curves were fitted by four exponential components and the fitting results are listed in Table 3. The two longer lifetimes (unit: ms) are ascribed to the $^4E(^2G) \rightarrow ^4A_g(^2F)$ transitions of Cr$^{3+}$ forbidden by spin-selection rules. The two shorter lifetimes (unit: µs) originate from the allowed $^4T_2(^4F) \rightarrow ^4A_g(^2F)$ transitions of Cr$^{3+}$. Since the surface Cr$^{3+}$ ions occupy the low-symmetry sites, this will result in a shorter decay time compared to the interior Cr$^{3+}$ ions. For the interior Cr$^{3+}$ existing in the undoped nanoparticles, the lifetimes related to the
Meanwhile, more anti-defects, such as $Zn_{Ga}^0$ and $Ga_{Zn}^0$, are formed after Pr$^{3+}$ doping and this will increase the nonradiative rate, $A_{nr}$, and quench the NIR emissions of the interior Cr$^{3+}$. Therefore, it can be deduced that the increased lifetimes from the $^4E(2G) \rightarrow ^4A_2(4F)$ and $^4T_{2}(4F) \rightarrow ^4A_2(4F)$ transitions of the interior Cr$^{3+}$ existing in the Pr$^{3+}$ doped nanoparticles are attributed to the decreased energy transfer rate. This energy transfer process under 575 nm excitation might be related to the energy transfer of the excited electrons from the $^2T_2(4F)$ level of Cr$^{3+}$ to the trap levels. Based on the theoretical study reported by De Vos et al., it was believed that there existed charge transfer between Cr$^{3+}$ and anti-site pairs ($Ga_{Zn}$ – $Zn_{Ga}$) in ZnGa$_2$O$_4$:Cr$^{3+}$.$^{26}$ Meanwhile, Gourier et al. also found that the local electric field at Cr$^{3+}$, created by the two neighboring anti-site pairs ($Ga_{Zn}$ – $Zn_{Ga}$) triggered electron–hole separation and trapping upon visible light excitation.$^{27}$ These theoretical and experimental results are consistent with our kinetics analysis. Thus, for the interior Cr$^{3+}$ ions existing in the ZGGO:Cr$^{3+}$:Pr$^{3+}$ nanoparticles, it can be inferred that the traps related to the energy transfer process might be linked to the anti-site pair ($Ga_{Zn}$ – $Zn_{Ga}$), which is close to the distorted Cr$^{3+}$ ions. For the surface Cr$^{3+}$ ions in the Pr$^{3+}$ doped nanoparticles, the Pr$^{3+}$ concentration-dependent lifetimes related to the $^4E(2G) \rightarrow ^4A_2(4F)$ transition show a similar increasing behavior to those of the interior Cr$^{3+}$ in the nanoparticles. However, after Pr$^{3+}$ doping, the decreased lifetimes might be attributed to the contribution of the increased radiative rate induced by the highly deformed surroundings of the distorted octahedral sites, occupied by Cr$^{3+}$, due to the spin-allowed $^4T_{2}(4F) \rightarrow ^4A_2(4F)$ transition.$^{28}$

To understand the effect of Pr$^{3+}$ doping on the persistent luminescence, the afterglow decay curves of NIR ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles (x = 0, 0.010, 0.020, 0.025) monitored at 697 nm after 5 min stopping 254 nm UV light irradiation for 10 min were obtained and are shown in Fig. 7. For all the samples, the afterglow time can reach 730 min, proved by the observed phosphorescence as shown in the inset of Fig. 7. In particular, the sample with x = 0.020 exhibits the maximum persistent luminescence intensity. Although the average grain size of the ZGGO:Cr$_{0.020}$Pr$_{0.020}$ nanoparticles is smaller than that of the undoped sample based on the TEM observation, its afterglow intensity is dramatically increased. According to the study reported by Bessière et al., it was found that the enhanced persistent luminescence was linked to the decreased Zn/Ga ratio (<50%), i.e. a nominal Zn-deficiency.$^{17}$ However, for each of our samples ($Zn_{2}Ga_{2.98}Ge_{0.75}O_{8}$:Cr$_{0.020}$Pr$_x$), the Zn/(Ga + Ge + Cr + Pr) ratio is larger than 50%, suggesting that no Zn-deficiency is found. Thus, the enhanced afterglow intensity does not originate from the change in the Zn/Ga ratio of the $Zn_{2}Ga_{2.98}Ge_{0.75}O_{8}$:Cr$_{0.020}$Pr$_x$ nanoparticles with different Pr$^{3+}$ concentrations. In our case, it might be related to the formation of more traps, such as anti-defects ($Ga_{Zn}$ and $Zn_{Ga}$) or anti-site pairs ($Ga_{Zn}$ – $Zn_{Ga}$), in the nanoparticles due to Pr$^{3+}$ doping.$^{9,29,30}$ The aforementioned results suggest that it is possible for Pr$^{3+}$ doping in the ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles not only to tune the particle size but also to increase the NIR persistent intensity and prolong the afterglow time.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Decay$^a$ (ms)</th>
<th>Decay$^b$ (µs)</th>
</tr>
</thead>
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<tr>
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<td>$\tau_s = 3.0$</td>
<td>$\tau_i = 7.6$</td>
</tr>
<tr>
<td>x = 0.010</td>
<td>$\tau_s = 3.9$</td>
<td>$\tau_i = 9.6$</td>
</tr>
<tr>
<td>x = 0.020</td>
<td>$\tau_s = 4.3$</td>
<td>$\tau_i = 10.9$</td>
</tr>
<tr>
<td>x = 0.025</td>
<td>$\tau_s = 4.0$</td>
<td>$\tau_i = 10.0$</td>
</tr>
</tbody>
</table>

The samples are ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles with different Pr$^{3+}$ doping concentrations (x = 0, 0.010, 0.020, 0.025).$^a$ The $^4E(2G) \rightarrow ^4A_2(4F)$ emission. $^b$ The $^4T_{2}(4F) \rightarrow ^4A_2(4F)$ emission. $\tau_s$ refers to the lifetime of the surface Cr$^{3+}$ ions in the nanoparticles. $\tau_i$ refers to the lifetime of the interior Cr$^{3+}$ ions in the nanoparticles.

$^3$E$(2G) \rightarrow ^4A_2(4F)$ and $^4T_{2}(4F) \rightarrow ^4A_2(4F)$ transitions are 7.6 ms and 685.1 µs, respectively. For those interior Cr$^{3+}$ ions existing in the Pr$^{3+}$ doped nanoparticles (x = 0.010, 0.020, 0.025), their lifetimes show an obviously increasing trend compared to the undoped sample (x = 0). Generally, the measured lifetime can be acquired according to the following equation:

$$\frac{1}{\tau} = A_{r} + A_{nr} + A_{t}$$

where $A_{r}$, $A_{nr}$ and $A_{t}$ are radiative, nonradiative and energy transfer rates of transition metal ions, respectively.$^{25}$ On the basis of the emission and Raman spectral analyses, the NIR emissions of the interior Cr$^{3+}$ in Pr$^{3+}$ doped nanoparticles are enhanced. If the enhanced emissions originate from the contribution of the increased radiative rate ($A_{r}$), decreased lifetimes of the interior Cr$^{3+}$ ions can be obtained. However, it is found that the above predicted result contradicts with the measured data (the increased lifetimes). Thus, the increased lifetimes cannot be attributed to the variation in the radiative rate.

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Fig. 6 Decay curves of Cr$^{3+}$ in ZGGO:Cr$_{0.020}$Pr$_x$ nanoparticles with different Pr$^{3+}$ doping concentrations (x = 0, 0.010, 0.020, 0.025). The monitoring and excitation wavelengths are 697 and 575 nm, respectively. The red lines represent the fitting data using a four exponential function.
To understand how Pr$^{3+}$ doping affects the traps, the TL glow curves of NIR ZGGO:Cr$^{0.020}$,Pr$^x$PLNPs with different amounts of Pr$^{3+}$ ($x = 0, 0.010, 0.020, 0.025$) were obtained and are shown in Fig. 8. For each of the samples, it can be seen that a broad TL peak around 330 K appears. In particular, the peak position slightly shifts towards a lower temperature with increasing Pr$^{3+}$ concentration from 0 to 0.020. In general, the trap depth ($E_t$) can be estimated using the following equation:

$$E_t (eV) = \frac{T_m}{500}$$

(2)

where $T_m$ corresponds to the temperature at the TL peak maximum, as shown in the inset of Fig. 8. Actually, the calculated trap depths decrease from 0.676 to 0.656 eV upon increasing the amount of Pr$^{3+}$ dopant from 0 to 0.020. On the basis of a reported work, the traps with a trap depth of $\sim 0.7$ eV might be associated with Ga$_{Zn}$Zn$_{Ga}$ anti-site pairs, which were close to Cr$^{3+}$ ions. Because Pr$^{3+}$ doping leads to the appearance of more anti-defects according the XPS and Raman analyses, the averaged distance between an anti-site pair and a Cr$^{3+}$ ion is decreased. Thus, it can be deduced that Pr$^{3+}$ doping will affect the trap depth, i.e. Pr$^{3+}$ doping will decrease the trap depth.

To illustrate the mechanism of the NIR persistent luminescence, the energy level diagram of Cr$^{3+}$ ions in ZGGO:Cr$_{0.020}$Pr$_x$ PLNPs with respect to the conduction band (CB) and the valence band (VB) is shown in Fig. 9. Under 254 or 320 nm UV excitation (process 1 or 2), the $^4A_2(^4F) \rightarrow ^4T_1(^4P)$ transition of Cr$^{3+}$ ions occurs through an energy transfer from the ZGGO host to Cr$^{3+}$ ions or a direct excitation of Cr$^{3+}$ ions. Based on previous studies, the origin of the NIR persistent luminescence (process 3) was ascribed to the thermal activation mechanism (processes 4–6), which was linked to the traps (trap$_1$ and/or trap$_2$). Meanwhile, upon 254 nm excitation, Abdukayum et al. believed that the excited electrons and holes in the host were captured by the native defects, which led to a broad blue emission at about 440 nm. This blue emission could induce $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ transitions of Cr$^{3+}$ ions via a new energy transfer (process 7). In the case of 575–590 nm excitation (process 8), the NIR persistent luminescence was attributed to the contribution of the tunneling processes (processes 9 and 10) related to the traps.
The NIR afterglow intensity of the sample containing Pr³⁺ (x = 0) is found to be different from that of the sample containing Pr³⁺ (x = 0.020). This is due to the change in the trap energy level resulting from the formation of more anti-defects.

In conclusion, Cr³⁺ and Pr³⁺ co-doped ZGOO NIR PLNPs with a spinel structure were prepared by a hydrothermal method along with a thermal annealing in a vacuum. These nanoparticles, the average particle size decreases from 64 to 37 nm with increasing Pr³⁺ doping concentration from 0 to 0.025 and Cr³⁺ and Pr³⁺ ions are uniformly doped in the interior and surface of a single nanoparticle. According to the X-ray photoelectron energy spectra (XPS) and Raman data, there exist more Ga and Zn species in both octahedral and tetrahedral sites in the Pr³⁺ doped ZGOO host compared to the undoped sample. In particular, Pr³⁺ doping dramatically promotes the formation of more anti-defects, Zn_Ga and Ga_Zn. From the emission and excitation spectra and the kinetics analysis, the strong NIR emissions around 697 nm are attributed to the 4A₂(4F) → 4A₂(4F) and 4T₂(4F) → 4A₂(4F) transitions of the interior and surface Cr³⁺ ions in the nanoparticles. In particular, the suppressed energy transfer of the excited electrons from the 4T₂(4F) level to the trap levels related to anti-site pairs (Ga_an – Zn_Ga) around distorted octahedral Cr³⁺ ions in the Pr³⁺ doped nanoparticles can be found. The enhanced NIR persistent luminescence of the Pr³⁺ doped ZGOO:Cr³⁺ nanoparticles at an optimal concentration is due to the formation of more anti-defects induced by Pr³⁺ doping. Our studies demonstrate that Pr³⁺ doped ZGOO:Cr³⁺ PLNPs have potential applications for bio-imaging.

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Notes and references
1. Y. Li and X. Yan, Nanoscale, 2016, 8, 14965–14970.