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Showcasing research from the Group of Prof. Yuxue Liu at School of Physics, Northeast Normal University, China and Prof. Hong Zhang at Van't Hoff Institute for Molecular Sciences, University of Amsterdam, The Netherlands.

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

The microstructure and optical properties of spinel-phase $\text{Zn}_2\text{Ga}_{2.98-x}\text{Ge}_{0.75}\text{O}_8:\text{Cr}_{0.020}\text{Pr}_x$ near infrared persistent luminescence nanoparticles are reported. Pr^{3+} doping leads to the appearance of more anti-site pairs ($\text{Ga}_{\text{Zn}}^{\circ} - \text{Zn}_{\text{Ga}}'$) around distorted octahedral Cr^{3+} ions and the enhanced 697 nm emissions of the interior and surface Cr^{3+} ions in the nanoparticles.

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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

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Spinel-phase $\text{Zn}_2\text{Ga}_{2.98-x}\text{Ge}_{0.75}\text{O}_8:\text{Cr}_{0.020}\text{Pr}_x$ (ZGGO:Cr³⁺,Pr³⁺) near infrared (NIR) persistent luminescence nanoparticles (PLNPs) with different amounts of Pr³⁺ 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 Pr³⁺ doping concentration from 0 to 0.025 and Cr³⁺ and Pr³⁺ ions are uniformly doped into the interior and surface of a single nanoparticle. It can be found that Pr³⁺ doping leads to the appearance of more anti-site pairs ($\text{Ga}_{\text{Zn}}^{\circ} - \text{Zn}_{\text{Ga}}'$) around distorted octahedral Cr³⁺ ions and enhanced NIR emissions around 697 nm, which originate from the $^2\text{E}(\text{G}) \rightarrow ^4\text{A}_2(\text{F})$ and $^4\text{T}_2(\text{F}) \rightarrow ^4\text{A}_2(\text{F})$ transitions of the interior and surface Cr³⁺ ions in the nanoparticles. In particular, for the interior Cr³⁺ ions in the Pr³⁺ 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 ($\text{Ga}_{\text{Zn}}^{\circ} - \text{Zn}_{\text{Ga}}'$) around the distorted octahedral Cr³⁺ ions. Our results suggest that Pr³⁺ doped ZGGO:Cr³⁺ PLNPs have potential applications for bio-imaging.

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Introduction

Novel NIR persistent luminescence materials emitting in the physiologically relevant “optical window” (650–950 nm) have attracted more and more attention due to their potential applications in clean energy resources and biomedicine.^{1–10} In particular, Pan *et al.* discovered bulk Cr³⁺-doped zinc gallogermanate (ZGGO) NIR persistent phosphors with an afterglow time longer than 360 h and predicted that they have promising applications in *in vivo* bio-imaging and solar energy use.⁸ Some therapeutic and/or diagnostic nanoplatforms were constructed using this kind of NIR persistent luminescence material. For example, Yang *et al.* prepared Cr³⁺-doped ZGGO nanoparticles with NIR emission at 697 nm and an afterglow time of more than 15 h and succeeded in realizing bio-imaging by dispersing them in human serum albumin solution.¹¹ Abdurahman *et al.* built a ZGGO:Cr³⁺ (core)/photosensitizer Si-Pc (shell) nanoplatform for photodynamic therapy and found enhanced NIR persistent luminescence by 808 nm re-excitation.²

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 *et al.* prepared rare earth ion double-doped ZGGO:Cr³⁺,Yb³⁺,Er³⁺ NIR PLNPs exhibiting a super-long afterglow time (> 20 days), low toxicity and excellent biocompatibility.¹ To achieve *in vivo* computed tomography and NIR luminescence bio-imaging, Lu *et al.* designed a ZGGO:Cr³⁺,Pr³⁺@TaO_x@SiO₂ nanoplatform.⁴ Abdukayum *et al.* also found that NIR Cr³⁺/Pr³⁺ codoped ZGGO PLNPs could be applied for *in vivo* targeted tumor imaging.⁷

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:Cr³⁺ 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 CaMgSi₂O₆:Eu²⁺,Mn²⁺,Pr³⁺, YPO₄:Pr³⁺,Ln³⁺ (Ln = Nd, Er, Ho, Dy) and ZGGO:Cr³⁺,Pr³⁺,

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praseodymium doping plays a key role in enhancing their persistent luminescence.^{7,9,12} Thus, spinel-phase ZGGO:Cr³⁺,Pr³⁺ 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:Cr³⁺,Pr³⁺ samples with different concentrations can be represented as Zn₂Ga_(4-x-y-z)Ge_zO₈:Cr_y,Pr_x, 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.¹¹

For these nanoparticles, our study indicates that the enhanced NIR persistent luminescence (around 697 nm) induced by Pr³⁺ doping is attributed to the increased interior and surface Cr³⁺ in the distorted octahedral sites and the suppressed energy transfer of the excited electrons from the ⁴T₂(⁴F) level to the trap levels related to anti-site pairs (Ga_{Zn}[•] – Zn_{Ga}[•]) around distorted octahedral Cr³⁺ ions. In particular, the average particle size was found to be dependent on Pr³⁺ doping concentration and tuned from 64 to 37 nm when the Pr³⁺ 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

Zn₂Ga_{2.98-x}Ge_{0.75}O₈:Cr_{0.020},Pr_x nanoparticles with different amounts of Pr³⁺ (*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(III) nitrate hydrate (99.9%) (Sigma-Aldrich), germanium(IV) chloride (99.99%) (Sigma-Aldrich), chromium(III) nitrate nonahydrate (99.95%) (Aladdin), and praseodymium(III) nitrate hexahydrate (99.99%) (Aladdin) with certain mole ratios was dissolved in deionized water with a successive stirring at pH = ~8.5. Then the colloidal solution was heated for 6 h at 183 °C in a Teflon-line steel autoclave (capacity: 40 ml). Subsequently, the obtained precipitates were repeatedly washed and dried at 73 °C for 5 h to acquire the as-prepared samples. The final samples with optimal persistent luminescence were obtained by annealing the as-prepared samples at 800 °C in a vacuum (pressure: ~2 × 10⁻³ Pa) for 1.5 h.

The X-ray diffraction (XRD) spectra were recorded with a Rigaku D/MAX-2500 X-ray diffraction spectrometer with Cu K α radiation (λ = 0.15418 nm). Compositions and morphologies of the samples were characterized by transmission electron microscopy (TEM) using a JEOL-2100F microscope (JEOL, Japan) operating at an acceleration voltage of 200 kV. The Raman spectra were recorded using a LabRAM HR Evolution Raman spectrometer (HORIBA) with 488 nm excitation. X-ray photoelectron energy spectra (XPS) were acquired using Al K α radiation (1486.6 eV) with a Thermo ESCALAB 250 electron energy spectrometer. Emission and excitation spectra were performed on a SHIMADZU RF-5301PC spectrophotometer. Afterglow decays were measured using a SHIMADZU RF-5301PC spectrophotometer or Zolix Omni λ -300 spectrophotometer equipped with

a R928 photomultiplier tube. Luminescence decays were recorded with an InnoLas laser (SpitLight 600) and an InnoLas optical parametric oscillator. Thermoluminescence (TL) spectra monitored at 697 nm were measured by using an RF-5301PC spectrophotometer at a heating rate of 10 K min⁻¹ in the 288–533 K temperature range. All the digital photographs were recorded using a Digital Single Lens Reflex camera.

Results and discussion

Fig. 1 shows the XRD patterns of ZGGO:Cr_{0.020},Pr_x powders with different amounts of Pr³⁺ (*x* = 0, 0.005, 0.010, 0.015, 0.020, 0.025). For all the samples, it can be found that the observed diffraction peaks match the standard ZnGa₂O₄ pattern with a spinel structure (JCPDS card 38-1240). Impurity phases, such as zinc oxide, gallium oxide, germanium oxide, chromium oxide and praseodymium oxide, are not detected, indicating the pure phase spinel structure of the ZGGO:Cr_{0.020},Pr_x samples. Since the radii of Cr³⁺ (0.62 Å) and Ge⁴⁺ (0.54 Å) ions are similar to the Ga³⁺ (0.62 Å) ionic radius, we believe that the Cr³⁺ and Ge⁴⁺ ions might substitute for Ga³⁺ ions located at octahedral sites in the ZnGa₂O₄ spinel structure. This is supported by the study reported by Allix *et al.*, who believed that different substitution elements, such as Cr³⁺, Ge⁴⁺ and Sn⁴⁺, almost occupied the octahedral sites in ZnGa₂O₄ materials.⁶ Although Pr³⁺ (0.99 Å) is much larger in radius than Ga³⁺ (0.62 Å), it is likely that Pr³⁺ ions tend to replace Ga³⁺ ions at the octahedral sites in ZGGO:Cr_{0.020},Pr_x powders.^{6,11,13,14}

To determine the grain size of the powders, TEM images of ZGGO:Cr_{0.020},Pr_x powders with different amounts of Pr³⁺ 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

Fig. 1 The XRD patterns of ZGGO:Cr_{0.020},Pr_x nanoparticles with different Pr³⁺ doping concentrations (*x* = 0, 0.005, 0.010, 0.015, 0.020, 0.025).

Fig. 2 (a–f) TEM photographs of ZGGO:Cr_{0.020},Pr_x nanoparticles with different Pr³⁺ doping concentrations ($x = 0, 0.005, 0.010, 0.015, 0.020, 0.025$). (g–l) EDS elemental mapping and (m) EDS of the ZGGO:Cr_{0.020},Pr_{0.020} nanoparticles. The enlarged EDS in the range of 0.4–1.4 eV is shown in the inset of (m).

Table 1 The fitting data related to the size distribution of ZGGO:Cr_{0.020},Pr_x nanoparticles with different Pr³⁺ doping concentrations ($x = 0, 0.005, 0.010, 0.015, 0.020, 0.025$)

Sample	Mean/nm	Standard deviation/nm
$x = 0$	64	20
$x = 0.005$	46	15
$x = 0.010$	44	16
$x = 0.015$	40	12
$x = 0.020$	40	13
$x = 0.025$	37	13

and an average particle size of ~ 64 nm exhibit an aggregated behavior. For the Pr³⁺ 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 Pr³⁺ doping. Our observation is consistent with the study reported by Wang *et al.*, who believed that the decreased size of Gd³⁺ doped NaYF₄:Yb/Er nanoparticles relative to the undoped sample was ascribed to

the strong influence of Gd³⁺ ions on the nanocrystal growth rate *via* surface charge modification.¹⁵ Thus, in our study, the decreased size of the ZGGO:Cr³⁺,Pr³⁺ nanoparticles might be linked to the substitution of Ga³⁺ by Pr³⁺. Pr³⁺ 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:Cr³⁺,Pr³⁺ nanoparticles can be controlled by adjusting Pr³⁺ 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 Cr³⁺ and Pr³⁺ 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 (Cr³⁺ and Pr³⁺) were also clearly observed.

To reveal the effect of Pr³⁺ doping on the surface distributions of Ga³⁺ and Zn²⁺ 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 Pr³⁺ ($x = 0, 0.010, 0.020, 0.025$) 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 Pr³⁺ 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 Ga³⁺ (B site) and Zn²⁺ (A site) ions in the ZGGO host with an AB₂O₄ 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 Ga³⁺ ions in the octahedral sites and Zn²⁺ 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 Ge⁴⁺ ($y = 0.75$) 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 (Zn²⁺ ions in the octahedral sites and Ga³⁺ ions in the tetrahedral sites) on the surface of the undoped sample. For each of the Pr³⁺ 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}

Fig. 3 (a and b) The Zn 2p_{3/2} and Ga 2p_{3/2} XPS of ZGGO:Cr_{0.020},Pr_x nanoparticles with different Pr³⁺ doping concentrations ($x = 0, 0.010, 0.020, 0.025$). (c) The coordination environments of Ga and Zn sites in ZGGO:Cr_{0.020},Pr_x PLNPs.

core levels for the ZGGO:Cr_{0.020},Pr_x nanoparticles with different amounts of Pr³⁺ are given in Table 2. After Pr³⁺ 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 Pr³⁺ 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 Zn'_{Ga} and Ga[°]_{Zn}.¹³ Thus, the appearance of more Zn'_{Ga} and Ga[°]_{Zn} anti-defects in ZGGO might be attributed to Pr³⁺ 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 Ga³⁺ ion and six or

Table 2 The binding energies of the Zn 2p_{3/2} and Ga 2p_{3/2} core-levels of ZGGO:Cr_{0.020},Pr_x PLNPs with different Pr³⁺ doping concentrations ($x = 0, 0.010, 0.020, 0.025$)

Sample	Zn 2p _{3/2}		Ga 2p _{3/2}	
	Peak ₁ ^a BE (eV)	Peak ₂ ^b BE (eV)	Peak ₁ ^a BE (eV)	Peak ₂ ^b BE (eV)
$x = 0$	1021.1	—	—	1117.9
$x = 0.010$	1021.1	1021.3	1117.3	1117.7
$x = 0.020$	1021.1	1021.2	1117.1	1117.5
$x = 0.025$	1021.0	1021.4	1117.4	1119.2

The samples are ZGGO:Cr_{0.020},Pr_x nanoparticles with different Pr³⁺ doping concentrations ($x = 0, 0.010, 0.020, 0.025$). ^a Peak₁ refers to the Zn 2p_{3/2} or Ga 2p_{3/2} peak, which corresponds to Zn²⁺ or Ga³⁺ in a tetrahedral site. ^b Peak₂ refers to the Zn 2p_{3/2} or Ga 2p_{3/2} peak, which corresponds to Zn²⁺ or Ga³⁺ in an octahedral site. BE represents binding energy.

four oxygen anions. Therefore Pr³⁺ doping could lead to the generation of distorted octahedra and tetrahedra in the ZGGO host.

To further unravel the effect of Pr³⁺ doping on the microstructure of the nanoparticles, Raman spectra of the ZGGO:Cr_{0.020},Pr_x nanoparticles with different amounts of Pr³⁺ ($x = 0, 0.010, 0.020, 0.025$) 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 Γ 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 ZnO₄ groups with symmetric stretching vibrations in the undoped sample ($x = 0$). Thus, it is possible to detect the

Fig. 4 Raman spectra of the spinel phased ZGGO:Cr_{0.020},Pr_x nanoparticles with different Pr³⁺ doping concentrations ($x = 0, 0.010, 0.020, 0.025$) upon 488 nm excitation.

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 $\text{Ga}_{\text{Zn}}^\circ$, 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.²⁰ 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 ($\lambda_{\text{ex}} = 590\text{ nm}$) and excitation ($\lambda_{\text{em}} = 697\text{ nm}$) spectra of $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ 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 ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ and ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions of Cr^{3+} ions in the distorted octahedral site, respectively.^{6,8,11} 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 $220\text{--}680\text{ nm}$ region. According to the Tanabe–Sugano diagram representing the octahedrally coordinated $3d^3$ ion system as shown in the inset of Fig. 5b, the excitation peak around 260 nm originates from the contributions of the ZGGO host and O–Ga charge transfer absorptions.^{8,21} Meanwhile, excitation peaks around $320, 440$ and 590 nm are ascribed to the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$, ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{F})$ and ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_2({}^4\text{F})$ transitions of Cr^{3+} , respectively.^{5,8,11} In particular, the appearance of the mixed 697 and 712 nm NIR emissions of the NIR $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ nanoparticles suggests that the luminescent center (Cr^{3+} ion) locates in a site with the intermediate field, *i.e.* the crossing point of the ${}^4\text{T}_2({}^4\text{F})$ and ${}^2\text{E}({}^2\text{G})$ levels.^{11,22,23}

To unravel how Pr^{3+} doping influences the surroundings of Cr^{3+} ions, luminescence decays of the 697 nm emission of $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ nanoparticles with different amounts of Pr^{3+}

Fig. 5 (a) Emission ($\lambda_{\text{ex}} = 590\text{ nm}$) and (b) excitation ($\lambda_{\text{em}} = 697\text{ nm}$) spectra of $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ nanoparticles with different Pr^{3+} doping concentrations ($x = 0, 0.010, 0.020, 0.025$). The Tanabe–Sugano diagram representing the octahedrally coordinated $3d^3$ ion system of Cr^{3+} is shown in the inset in (b).

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.¹¹ 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 ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions of Cr^{3+} forbidden by spin-selection rules.²⁴ The two shorter lifetimes (unit: μs) originate from the allowed ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ 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.¹¹ For the interior Cr^{3+} existing in the undoped nanoparticles, the lifetimes related to the

Fig. 6 Decay curves of Cr^{3+} in $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ 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.

Table 3 The lifetimes of NIR emissions of $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ nanoparticles with different Pr^{3+} doping concentrations ($x = 0, 0.010, 0.020, 0.025$) upon 575 nm excitation

Sample	Decay ^a (ms)		Decay ^b (μs)	
$x = 0$	$\tau_s = 3.0$	$\tau_i = 7.6$	$\tau_s = 68.2$	$\tau_i = 685.1$
$x = 0.010$	$\tau_s = 3.9$	$\tau_i = 9.6$	$\tau_s = 54.9$	$\tau_i = 1058.4$
$x = 0.020$	$\tau_s = 4.3$	$\tau_i = 10.9$	$\tau_s = 66.3$	$\tau_i = 1065.6$
$x = 0.025$	$\tau_s = 4.0$	$\tau_i = 10.0$	$\tau_s = 87.1$	$\tau_i = 1088.1$

The samples are $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ nanoparticles with different Pr^{3+} doping concentrations ($x = 0, 0.010, 0.020, 0.025$). ^a The ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ emission. ^b The ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ emission. τ_s refers to the lifetime of the surface Cr^{3+} ions in the nanoparticles. τ_i refers to the lifetime of the interior Cr^{3+} ions in the nanoparticles.

${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ and ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ 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:

$$1/\tau = A_r + A_{nr} + A_{tr} \quad (1)$$

where A_r , A_{nr} and A_{tr} 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.

Meanwhile, more anti-defects, such as Zn'_{Ga} and $\text{Ga}^\circ_{\text{Zn}}$, 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 ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ and ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ 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 ${}^4\text{T}_2({}^4\text{F})$ 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 ($\text{Ga}^\circ_{\text{Zn}} - \text{Zn}'_{\text{Ga}}$) in $\text{ZnGa}_2\text{O}_4\text{Cr}^{3+}$.²⁶ Meanwhile, Gourier *et al.* also found that the local electric field at Cr^{3+} created by the two neighboring anti-site pairs ($\text{Ga}^\circ_{\text{Zn}} - \text{Zn}'_{\text{Ga}}$) 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 $\text{ZGGO:Cr}^{3+}, \text{Pr}^{3+}$ nanoparticles, it can be inferred that the traps related to the energy transfer process might be linked to the anti-site pair ($\text{Ga}^\circ_{\text{Zn}} - \text{Zn}'_{\text{Ga}}$), 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 ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ 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 ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transition.²⁸

To understand the effect of Pr^{3+} doping on the persistent luminescence, the afterglow decay curves of NIR $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ 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 $\text{ZGGO:Cr}_{0.020}\text{Pr}_{0.020}$ 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 ($\text{Zn}_2\text{Ga}_{2.98-x}\text{Ge}_{0.75}\text{O}_8\text{Cr}_{0.020}\text{Pr}_x$), the $\text{Zn}/(\text{Ga} + \text{Ge} + \text{Cr} + \text{Pr})$ 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 $\text{Zn}_2\text{Ga}_{2.98-x}\text{Ge}_{0.75}\text{O}_8\text{Cr}_{0.020}\text{Pr}_x$ nanoparticles with different Pr^{3+} concentrations. In our case, it might be related to the formation of more traps, such as anti-defects ($\text{Ga}^\circ_{\text{Zn}}$ and Zn'_{Ga}) or anti-site pairs ($\text{Ga}^\circ_{\text{Zn}} - \text{Zn}'_{\text{Ga}}$), 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 $\text{ZGGO:Cr}_{0.020}\text{Pr}_x$ nanoparticles not only to tune the particle size but also to increase the NIR persistent intensity and prolong the afterglow time.

Fig. 7 NIR afterglow decay curves ($\lambda_{\text{mon}} = 697$ nm) of ZGGO:Cr_{0.020},Pr_x PLNPs with different Pr³⁺ doping concentrations ($x = 0, 0.010, 0.020, 0.025$) after 254 nm irradiation for 10 min. The inset shows phosphorescence spectra of the samples acquired at 730 min after stopping the UV irradiation.

To understand how Pr³⁺ doping affects the traps, the TL glow curves of NIR ZGGO:Cr_{0.020},Pr_x PLNPs with different amounts of Pr³⁺ ($x = 0, 0.010, 0.020, 0.025$) 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 Pr³⁺

Fig. 8 TL spectra of ZGGO:Cr_{0.020},Pr_x nanoparticles with different Pr³⁺ doping concentrations ($x = 0, 0.010, 0.020, 0.025$) after 254 nm irradiation for 5 min. The heating rate was ~ 10 K min⁻¹. The inset shows the temperature at the maximum of TL peaks and the corresponding trap depths.

concentration from 0 to 0.020. In general, the trap depth (E_t) can be estimated using the following equation:

$$E_t \text{ (eV)} = T_m/500 \quad (2)$$

where T_m corresponds to the temperature at the TL peak maximum, as shown in the inset of Fig. 8.³¹ Actually, the calculated trap depths decrease from 0.676 to 0.656 eV upon increasing the amount of Pr³⁺ dopant from 0 to 0.020. On the basis of a reported work, the traps with a trap depth of ~ 0.7 eV might be associated with Ga_{Zn}^o – Zn_{Ga}ⁱ anti-site pairs, which were close to Cr³⁺ ions.^{5,6,13} Because Pr³⁺ doping leads to the appearance of more anti-defects according to the XPS and Raman analyses, the averaged distance between an anti-site pair and a Cr³⁺ ion is decreased. Thus, it can be deduced that Pr³⁺ doping will affect the trap depth, *i.e.* Pr³⁺ doping will decrease the trap depth.

To illustrate the mechanism of the NIR persistent luminescence, the energy level diagram of Cr³⁺ 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 ⁴A₂(⁴F) → ⁴T₁(⁴P) transition of Cr³⁺ ions occurs through an energy transfer from the ZGGO host to Cr³⁺ ions or a direct excitation of Cr³⁺ 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 (trap₁ and/or trap₂).^{8,11} Meanwhile, upon 254 nm excitation, Abdulkayum *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 ⁴A₂(⁴F) → ⁴T₁(⁴F) transitions of Cr³⁺ ions *via* a new energy transfer (process 7).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

Fig. 9 The schematic diagram for the persistent NIR luminescence mechanism of the ZGGO:Cr_{0.020},Pr_x PLNPs. CB and VB stand for the conduction and valence bands, respectively.

(trap₂ and trap₃).^{11,32} The aforementioned result is consistent with the kinetics analysis, suggesting that the trap₃ level might be related to an anti-site pair ($\text{Ga}_{\text{Zn}}^{\circ} - \text{Zn}_{\text{Ga}}^{\prime}$), which is close to a distorted Cr^{3+} ion. According to the first-principles study reported by De Vos *et al.*, the change in defect energy for anti-site pairs around Cr^{3+} in ZnGa_2O_4 depends on the location of the constituting anti-sites, $\text{Zn}_{\text{Ga}}^{\prime}$ and $\text{Ga}_{\text{Zn}}^{\circ}$, with respect to chromium, and their mutual distances to each other.²⁶ By combining the TL analysis, it is found that Pr^{3+} doping leads to a decrease of the averaged distance between an anti-site pair and a Cr^{3+} ion. Thus, it can be deduced that Pr^{3+} doping can lead to the change in the trap depths, *i.e.* the decreased trap depths. This will suppress the energy transfer from the $^4\text{T}_2(^4\text{F})$ level to the trap₃ level and enhance NIR persistent luminescence of the $\text{ZGGO}:\text{Cr}_{0.020},\text{Pr}_x$ PLNPs.

To demonstrate how Pr^{3+} doping influences bio-imaging using $\text{ZGGO}:\text{Cr}_{0.020},\text{Pr}_x$ PLNPs after NIR light penetrating local tissue, a 5 mm thick pork slice as shown in Fig. 10a and b was placed between two discs, which were pressed by Cr^{3+} doped ZGGO powders without Pr^{3+} ($x = 0$) and containing Pr^{3+} ($x = 0.020$) powders, respectively, and a detector (a digital camera). The clear images of the two discs were observed under white light excitation as shown in Fig. 10c. However, the red images of the disc containing Pr^{3+} are brighter than those without Pr^{3+} at different afterglow times (0, 5, 10, 20 s) after stopping 254 nm light irradiation as shown in Fig. 10d–g. This is proved by the time-dependent afterglow intensity of the two samples as shown in Fig. 10h, where the NIR afterglow intensity of the sample containing Pr^{3+} is twice as strong as that of the sample without Pr^{3+} covered with a 5 mm thick pork slice at different afterglow times after stopping 254 nm irradiation. In addition, for the two discs, the red distorted images are attributed to the non-uniform distribution of the pork tissue which led to different

penetrating depths of NIR light (~ 697 nm). In a word, our results suggest that chromium and praseodymium codoped ZGGO persistent luminescence nanoparticles have potential applications in *in vivo* bio-imaging.

Conclusions

In sum, Cr^{3+} and Pr^{3+} co-doped ZGGO NIR PLNPs with a spinel structure were prepared by a hydrothermal method along with a thermal 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 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 Pr^{3+} doped ZGGO host compared to the undoped sample. In particular, Pr^{3+} doping dramatically promotes the formation of more anti-defects, $\text{Zn}_{\text{Ga}}^{\prime}$ and $\text{Ga}_{\text{Zn}}^{\circ}$. From the emission and excitation spectra and the kinetics analysis, the strong NIR emissions around 697 nm are attributed to the $^2\text{E}(^2\text{G}) \rightarrow ^4\text{A}_2(^4\text{F})$ and $^4\text{T}_2(^4\text{F}) \rightarrow ^4\text{A}_2(^4\text{F})$ transitions of the interior and surface Cr^{3+} ions in the nanoparticles. In particular, the suppressed energy transfer of the excited electrons from the $^4\text{T}_2(^4\text{F})$ level to the trap levels related to anti-site pairs ($\text{Ga}_{\text{Zn}}^{\circ} - \text{Zn}_{\text{Ga}}^{\prime}$) around distorted octahedral Cr^{3+} ions in the Pr^{3+} doped nanoparticles can be found. The enhanced NIR persistent luminescence of the Pr^{3+} doped ZGGO: Cr^{3+} nanoparticles at an optimal concentration is due to the formation of more anti-defects induced by Pr^{3+} doping. Our studies demonstrate that Pr^{3+} doped ZGGO: Cr^{3+} PLNPs have potential applications for bio-imaging.

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Fig. 10 Digital photos of a 5 mm thick pork slice (a and b) and two discs containing Pr^{3+} and without Pr^{3+} (c) under white light illumination. (d–g) The NIR images of two phosphor pieces were taken at different afterglow times (5 to 20 s) after stopping the 254 nm irradiation. (h) NIR afterglow decay curves (monitored at 697 nm) of the $\text{ZGGO}:\text{Cr}_{0.020}$ and $\text{ZGGO}:\text{Cr}_{0.020},\text{Pr}_{0.020}$ nanoparticles covered with a 5 mm thick pork slice after stopping the 10 min irradiation with 254 nm UV light. Imaging parameters: a–c, auto/ISO 400/1/125 s; d–g, manual/ISO 6400/0.3 s.

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