Visible and ultraviolet upconversion and near infrared downconversion luminescence from lanthanide doped La$_2$Zr$_2$O$_7$ nanoparticles

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ABSTRACT

Single materials which have a multitude of photophysical processes by selective doping are in high demand in the community of material science due to their multifunctional applications. Upconversion (UC) and down-conversion (DC) luminescence properties of lanthanide doped nanoparticles (NPs) are imperative for their broad application potentials. Here, we describe two series of either doubly or triply doped La$_2$Zr$_2$O$_7$ NPs synthesized by a molten salt method. For the former, La$_2$Zr$_2$O$_7$:Yb,Er NPs display bright red and moderate green UC (VUC) and NIR-B DC (NDC) at around 1550 nm, which are highly desirable for in-vivo bioimaging applications. For the latter, La$_2$Zr$_2$O$_7$:Gd,Yb,Tm NPs demonstrate ultraviolet UC (UVUC) which can be exploited for water purification. In addition, we systematically investigated the effects of sensitizer doping level on the morphology, crystal structure and UC and DC emission intensity of these NPs. The processes involved in the VUC, NDC and UVUC emissions are evaluated in detail by pump power dependence studies which reveal that the VUC emissions are two-photon processes whereas the UVUC emission is a five-photon absorption process. The mechanisms of all these three luminescence processes have been extensively explained based on energy transfer and f-f transition processes. The idea provided in this work extends the knowledge on doping induced UC and DC luminescence in pyrochlore NPs which show multifunctionalities in light emission properties.

1. Introduction

An upconversion (UC) process involves photons emitted with higher frequency than those being used as pumping photons [1,2]. There are several mechanisms which contribute to UC process: ground state absorption followed by excited-state absorption, sequential energy transfer, combination of the former and the latter, photon avalanche, cooperative UC [3–6]. Near infrared (NIR) to visible UC materials have been in great demand in recent years due to their unique anti-Stoke optical features that can be implemented in three-dimensional displays [7], laser and optical amplifiers [8], solar cells [9], optical data storage [10], bio-technologies [11,12], drug-delivery, biosensor, super resolution microscopy, optical temperature sensors [13,14], etc. At the meantime, IR to UVUC materials have also received intensive attention recently due to the applications of UV light in the areas of water disinfection, microbial inactivation, counterfeit detection, lithography, phototherapy, coating technology, forensics, etc. [15,16].

Currently UC materials face the issue of low luminescence efficiency [17,18]. The selective use of sensitizing and activating ions with close intermediate-excited states is essential to enhance UC efficiency [19,20]. Proper design and optimization of the interaction between sensitizer and activator ions is needed since UC efficiency is highly dependent on the separation distance of dopants.

Trivalent erbium and ytterbium have been widely used for UC materials [13,17,21–23]. The former is one of the most widely explored activators for UC process as it can be efficiently pumped using 980 nm laser to higher energy levels viz. $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_9$ [24]. The latter is used as a sensitizer to improve the efficiencies and absorptions of 980 nm laser because it only possesses one excited f-electron level to allow a strong and broad absorption band at 980 nm [22]. The Er$^{3+}$–Yb$^{3+}$ combination has been used to improve absorption cross-section of 980 nm photons because Yb$^{3+}$ ions sensitize Er$^{3+}$ ions to upper energy levels through energy transfer.

Moreover, host materials have been triple doped for NIR excitation to UVUC emission, e.g. Yb$^{3+}$, Gd$^{3+}$ and Tm$^{3+}$ with different concentrations [16,25–27]. These doping ions have been selected due to their exclusive properties. Tm$^{3+}$ has appropriate metastable levels for UVUC emission through the single transition of $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$. Yb$^{3+}$ is...
selected as sensitizer for Tm$^{3+}$ activator because of its sole excited energy level to generate large UC improvement and effective UVUC emissions [28–30]. It is difficult to directly populate Gd$^{3+}$ excited energy levels by IR pumping due to the large energy gap between its ground state $^{8}$S$_{7/2}$ and the first excited state $^{8}$P$_{5/2}$ [16]. To resolve this issue, introduction of Tm$^{3+}$ and Yb$^{3+}$ to Gd$^{3+}$ doped materials offers additional UVUC emissions essential for the development of UV compact devices [31,32].

On the other hand, NIR-A $\rightarrow$ NIR-B downconversion (DC) luminescent materials absorb the NIR-A light ($\sim$ 700–1000 nm) and emit in the NIR-B region ($\sim$ 1100–1700 nm). This type of materials such as quantum dots (QDs), carbon nanotubes (CNTs) and polymeric nanoparticles (NPs) are potential candidates for deep tissue imaging [33–35]. Such unique characteristics arise from the presence of narrow band gaps of these materials. The reported materials in this class such as CNTs and QDs suffer from the photobleaching problem which is highly undesirable for in vivo fluorescence imaging [36]. Another problem with the NIR emitting QDs is that they consist of highly toxic elements such as Pb, As, Hg, etc. [37] CNTs have problems for multi-spectral analysis and disease-specific imaging in the NIR based imaging along with the requirements of high-power pulsed sources (> 2 W) and long camera exposure [38–40]. Moreover, most of the materials in this category emit in the region < 1400 nm (NIR-B1) [34,41]. Materials with emission in the NIR-B2 region ($\sim$1500–1600 nm) allow improved scattering and H$_2$O absorption. However, materials emitting in the NIR-B2 region are rarely reported.

La$_2$Zr$_2$O$_7$ (LZO) has a pyrochlore structure with wide band gap, high structural stability, high dielectric constant, optimum refractive index, ability of accommodate lanthanide ions easily at both A and B sites, high thermal stability, etc. [43] In addition, it possesses a relatively low phonon energy at $\sim$785 cm$^{-1}$ which minimizes nonradiative relaxation while boosting quantum efficiency [44]. It is reported that A$_2$B$_2$O$_7$ type ordered pyrochlores (Fd3m) undergo phase transition to disordered fluorite phase (Fm3m) or vice versa by varying temperature, pressure, ionizing radiation, and chemical doping [45–47]. Radius ratio of the A and B cations ($r_A/r_B$) plays a decisive role between its disordered fluorite (DF) $\leftrightarrow$ ordered pyrochlore (OP) phase transition. The OP phase is stable when the $r_A/r_B$ value is $\geq$ 1.46 whereas the DF phase is stable when the $r_A/r_B$ value is $< 1.46$. Both phases have their own advantages: the OP phase is found to be suitable for sensing, scintillator, and thermal barrier coating applications whereas the DF phase is found to be ideal for nuclear waste host and ionic conductor applications [45,46,48,49]. In the literature, alluvialom doping of A$_2$B$_2$O$_7$ pyrochlores has induced pyrochlore-to-fluorite/cotunnite structural transition [46,50]. In terms of UC emission, La$_2$Zr$_2$O$_7$ has shown red/green UC after replacing Zr by Si [51].

In this work, we report the development of doubly and triply doped LZO nanoparticles (NPs) by a facile molten salt synthesis method [43,46,52,53]. These NPs show efficient VUC and UC and excellent NIR-B2 emission in the 1475–1600 nm under 980 nm excitation with negligible photobleaching. We have investigated the effects of sensitizer concentration on structure, size and photophysical properties of the doped LZO NPs. Specifically, for the doubly doped La$_2$Zr$_2$O$_7$:Yb,Er NPs, we have fixed the Er$^{3+}$ concentration at 3.0% (Figure S1) and varied the Yb$^{3+}$ concentration in the range of 0.25%–10.0%. The reason for this practice stems from the focus for UC relevant studies which have explored the effect of sensitizer ion while keeping the concentration of the main luminoophores in the range of 1–3% to avoid concentration quenching [54–57]. For similar reason, for the triply doped La$_2$Zr$_2$O$_7$:Gd,Yb,Tm NPs, we have fixed Yb$^{3+}$ concentration at 20%, Tm$^{3+}$ concentration at 1% and Gd$^{3+}$ concentration at 20% [31,32,58]. At the same time, power dependence of UC and DC emission intensity was investigated to give more insight on photon absorption process. The underlying mechanisms of light emission in all three VUC, NDC and UUC processes are explained extensively using energy transfer process and various f-f transitions.

2. Experimental

Synthesis and experimental details are included in the Electronic Supplementary Information.

3. Results and discussion

3.1. X-ray diffraction

XRD patterns of the doubly doped La$_2$Zr$_2$O$_7$:Er,Yb NPs with various sensitizer Yb$^{3+}$ concentrations and La$_2$Zr$_2$O$_7$:Yb,Tm,Gd NPs (Fig. 1a) showed that no other visible impure phases such as La$_2$O$_3$, Yb$_2$O$_3$, Er$_2$O$_3$, Tm$_2$O$_3$, Gd$_2$O$_3$ and ZrO$_2$ were detected. According to the XRD patterns, these samples are assigned to the pure La$_2$Zr$_2$O$_7$ phase with ideal pyrochlore structure (JCPDS No. 78–1292) with Fd-3m space group.

The crystallite size was calculated from the XRD data using the Debye-Scherer formula:

$$d = \frac{k\lambda}{\sqrt{(B_1^2 - B_2^2)\cos^2\theta}}$$

(1)
where \( d \) is the crystallite size, \( \lambda \) is the used X-ray wavelength, \( \theta \) is the angle of the corresponding Bragg reflection, which is fitted to calculate the full width half maxima (FWHM), \( B \) is the FWHM in radian, and \( K \) is the Scherer constant of 0.94 based on cubic crystallites. The FWHM was determined based on the XRD peak (222) with the highest intensity at 28.96° and the fitting was performed using pseudo voigt function. The \( B_{M} \) was calculated using the FWHM value of the highest intensity peak of pure silicon. The calculated crystallite size of the LZO::3%Er,y%Yb NPs (Table 1) decreases with increasing sensitizer concentration. This phenomenon is mainly attributed to the smaller ionic radius of 8-coordinated \( \text{Yb}^{3+} \) ion (98.6 p.m.) compared to 8-coordinated \( \text{La}^{3+} \) (116 p.m.).

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated Crystalline Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LZO03Er0.25Yb</td>
<td>22.1 ± 0.9</td>
</tr>
<tr>
<td>LZO03Er0.50Yb</td>
<td>20.9 ± 0.9</td>
</tr>
<tr>
<td>LZO03Er0.75Yb</td>
<td>19.9 ± 0.9</td>
</tr>
<tr>
<td>LZO03Er1Yb</td>
<td>15.0 ± 1.1</td>
</tr>
<tr>
<td>LZO03Er2Yb</td>
<td>13.5 ± 1.1</td>
</tr>
<tr>
<td>LZO03Er5Yb</td>
<td>12.3 ± 1.2</td>
</tr>
<tr>
<td>LZO03Er7Yb</td>
<td>10.9 ± 1.3</td>
</tr>
<tr>
<td>LZO03Er10Yb</td>
<td>9.6 ± 1.4</td>
</tr>
<tr>
<td>LZO02Yb1Tm20Gd</td>
<td>20.5 ± 0.3</td>
</tr>
</tbody>
</table>

Using common XRD to differentiate structures with similar space group can become difficult. The presence of weak reflections from the ordered pyrochlore phase cannot be ruled out from the XRD patterns of the LZO NPs (Fig. 1a). In this sense, Raman spectroscopy is a more sensitive technique to distinguish the disordered fluoride and ordered pyrochlore structures of LZO by probing metal-oxygen (\( M-O \)) vibrational modes [46,52]. A pyrochlore phase has a total of 6 Raman active vibrational modes existing in the wavenumber range of 200–1000 cm\(^{-1}\) which are \( \Gamma_{\text{OPP}} = A_{1g} + E_{g} + 4F_{2g} \), while the disordered fluoride structure has one active Raman mode that is \( \Gamma_{\text{DFP}} = F_{2g} \) because all seven \( \text{O}^{2-} \) ions are randomly oriented over the 8 anionic sites in this particular phase [53,59]. Phase transition from pyrochlore \( \text{A}_{2}\text{B}_{2}\text{O}_{6}\text{O}' \) phase (\( Fd3m \) space group, \( Z = 8 \)) to fluorite \( \text{AO}_{2}\text{F} \) structure (\( Fm\overline{3}m \), \( Z = 4 \)) proceeds by the disappearance of \( A_{1g} \) and \( E_{g} \) Raman modes and decrease in the number of \( F_{2g} \) mode from 4 to 1. The doubly doped LZO::3%Er,y%Yb NPs and the triply doped LZO::20%Yb,1.0%Tm,20%Gd NPs displayed 6 peaks corresponding to ideal pyrochlore structure (Fig. 1b). These peaks are located at 300, 395, 432, 495, 504 and 644 cm\(^{-1}\) corresponding to \( F_{2g} \), \( E_{g} \), \( F_{2g} \), \( A_{1g} \), \( F_{2g} \) and \( F_{2g} \) modes, respectively [43,60]. The Raman modes at 300, 395 and 432 cm\(^{-1}\) arise from the vibrations of the \( \text{La}–\text{O} \) and \( \text{Zr}–\text{O} \) bonds. The bands around 495, 504 and 644 cm\(^{-1}\) arise due to the stretching of the \( \text{Zr}–\text{O} \) bonds [45]. The extent of disordering from the LZO::3%Er,y%Yb NPs as a function of \( \text{Yb}^{3+} \) doping level can be predicted based on the variation of the full width half maxima (FWHM) of the most intense \( F_{2g} \) Raman peak.

![Fig. 2. SEM images of the LZO::3%Er,y%Yb NPs with different \( \text{Yb}^{3+} \) concentrations of (a) 0.25%, (b) 0.50%, (c) 0.75%, (d) 1.0%, (e) 2.0%, (f) 5.0%, (g) 7.0%, and (h) 10.0%, and (i) the LZO::20%Yb,1.0%Tm,20%Gd NPs.](image-url)
located around 300 cm⁻¹ [45]. The continuous increase of the FWHM value (Fig. 1b) suggests that the ordering extent of our LZO:3%Er:y%Yb NPs with the increasing Yb³⁺ concentration [45]. This phenomenon can be attributed to the tunneling of some Yb³⁺ ion from La³⁺ site to Zr⁴⁺ site at high Yb³⁺ concentration since the ionic radius of 6-coordinated Zr⁴⁺ ion is 72 p.m. whereas that of Yb³⁺ ion is 96.8 p.m [52]. Also, the ionic charge of these two ions is different. Such a mismatch of ionic charge and radius creates strain and lattice disordering and hence the broadening of the Raman peak [46,52,53].

3.3. Scanning electron microscopy

SEM was used to monitor the morphological features of the NPs synthesized using the molten-salt method. The doubly doped LZO:3% Er:y%Yb NPs are fine and monodispersd spheres with some extent of agglomeration (Fig. 2a-h). The size is in the range of 10–35 nm, which decreases from 37 nm to 24 nm as the Yb³⁺ concentration increases from 0.25% to 10%. The triply doped LZO:20%Yb,1.0%Tm,20%Gd NPs are spheres with an average size around 43 nm (Fig. 2i).

3.4. PL of the doubly doped LZO: 3%Er:y%Yb NPs

3.4.1. NIR-visible UC

The UC emission spectra of the LZO:Er, Yb NPs were recorded between 500 and 700 nm under 980 nm laser excitation (Fig. 3a). The three prominent peaks around 525, 550 and 660 nm are ascribed to the interconfigurational f-f transitions of Er³⁺. The dual bands at 525 and 550 nm in the green region are attributed to H₁₁/₂ → I₁₅/₂ and S₅/₂ → I₁₅/₂ transitions of Er³⁺ ion. The most intense band in the red region around 660 nm is due to F₀₂ → I₁₅/₂ transition of Er³⁺ ion. No obvious change of the spectral profile was observed as the of Yb³⁺ doping levels increases. This observation suggests that no substantial clustering of Er³⁺ and Yb³⁺ ions happened which could cause deactivation of Er³⁺ excited levels via non-radiative energy transfer [24]. The integral emission intensity ratio of the red and green emission bands varies with Yb³⁺ doping concentration, more specifically, increases initially up to 2.0% and thereafter gradually decreases till 10.0% (inset of Fig. 3a). A comparative UC emission spectrum for LZO:3%Er:y%Yb NPs with different Yb³⁺ concentrations was also performed. In terms of the variance of the red and green emission intensity with Yb³⁺ doping concentration, there is no spectral profile change while the UC emission intensity enhances (Fig. 3c). To predict the number of photons involved for Yb³⁺ to Er³⁺ energy transfer, the UC emission intensity varies with laser power following a relation [61]:

I ∝ P^n

where I is the integral area of a UC emission band, P is the laser power, and n is the number of photons involved in the excitation process and is calculated from the slope of log(I) vs log(P) linear plot.

The linear logarithmic plots of the integral area of each UC emission band (525, 550 and 660 nm) and the laser power of the LZO:3%Er:1% Yb NPs (Fig. 3d) show that there are linear relations between the UC intensity as a function of laser power. The slopes of the green emission bands (525 and 550 nm) and red band (660 nm) are approximately 2.0 indicating that two photons are needed to be absorbed by the LZO:3%Er:1%Yb NPs for generating green and red emissions. The correlation coefficient for all the three linear plots was approximately around 0.995 R². The CIE color coordinates of the LZO:3%:Er:1%:Yb NPs at laser power of 2.5 mW (Fig. 3e) with the highest emission output displayed yellowish green emission. There is no much change of either of these two values (Table S1).

The two main UC mechanisms in the excited state populations are energy transfer upconversion (ETU) and excited state absorption (ESA). Other mechanisms such as an avalanche process or cross-relaxation (CR) between two doped ions may also occur [62]. In general, ESA process is the dominant process for phosphors with low dopant concentrations given that it involves only one ion. On the other hand, ETU is dominant for phosphors with high dopant concentrations because it transfers the energy of between two close ions. High doping concentration decreases the average distance between dopant ions which enhances the interionic interaction [55].

The energy levels diagram of Er³⁺ and Yb³⁺ ions with the proposed UC processes of the LZO:Er³⁺, Yb³⁺ NPs is shown in Fig. 3f. Energy transfer from Yb³⁺ to Er³⁺ makes the largest contribution to the emission energy levels because Yb³⁺ has a large absorption cross section at the NIR region and a high doping concentration. Specifically, after absorbing 980 nm photon, Yb³⁺ ions go to excited 2F₇/₂ state and then relax to 1H₁₁/₂ level of Er³⁺ ions through energy transfer (ETU) due to the close energy between these two states. The absorption of the second photon cause the excitation of electron from 1H₁₁/₂ level of Er³⁺ to 2F₇/₂ levels. Then the electrons at the high energy 2F₇/₂ state decay nonradiatively to lower levels dissipating 525 and 550 nm green light from 1H₁₁/₂ and 5S₁₁/₂ respectively and red emission from states 5P₀₂.

Moreover, the red emission from the 5P₀₂ energy level is associated with two different processes. The first process is a nonradiative transition from 5P₁₂ → 5F₁₂ as described above. The second process is the population of 1I₁₃/₂ level through nonradiative transitions of 4I₁₁/₂ → 1I₁₃/₂, then the latter excited state is further promoted to 2F₇/₂ level either through an ET process as 5F₇/₂ (Yb³⁺) + → 2F₇/₂ (Yb³⁺) + → 5F₀₂ (Er³⁺) or an ESA process as photon + 1I₁₃/₂ (Er³⁺) → 4I₁₅/₂ (Er³⁺) + 5P₀₂ (Er³⁺) [63].

3.4.2. NIR-A to NIR-B DC

The process which involves NIR excitation and NIR fluorescence in the short wave infrared region (SWIR) is an excellent optical probe for fluorescence based in-vivo bioimaging [35,36,38,39,42]. Apart from the UC visible emissions in green and red regions, our LZO:Er, Yb NPs show intense broad spectral band around 1550 nm in NIR-B region under 980 nm excitation. For example, the LZO:3%Er:Yb:Yb NPs show intense broad NIR-B emission around 1550 nm which is split into several peaks (Fig. 4a). Such NIR-B emission peak is attributed to 4I₁₁/₂ → 4I₁₅/₂ Transition of Er³⁺ (Fig. 3f) and the large Stark splitting is cause by crystalline LZO environment [24]. Such DC process involves the excitation of Yb³⁺ by 980 nm photons from its ground 2F₇/₂ level to its single excited 2F₇/₂ level which relaxes to 4I₁₁/₂ level of Er³⁺ ion through ET. High energy states decay nonradiatively to lower 1I₁₃/₂ level of Er³⁺ ion followed with emission at 1550 nm due to electronic transition from 1I₁₃/₂ to 1I₁₅/₂ [64]. Moreover, the DC emission intensity increases with increasing Yb³⁺ concentration up to 5.0 mol% of Yb³⁺ and then gradually decreases due to concentration quenching (Fig. 4b).

3.5. PL of the triply doped LZO:Yb,Tm,Gd NPs

The LZO:20%Yb,1%Tm,20%Gd NPs displayed UV UC fluorescence under 980 nm excitation (Fig. 5a). The emission peak centered at 289 nm is assigned to the P₂⁰→₁⁰ H₆ transition of Tm³⁺. Emissions peaked at 296, 300, 306 nm are originated from P₂⁰→₁⁰ S₂⁰, P₂⁰→₁⁰ S₂⁰ and P₂⁰→₁⁰ S₂⁰ transitions of Gd³⁺ ion, respectively [32]. Fig. 5b shows the energy levels diagram of the Yb³⁺, Gd³⁺, and Tm³⁺ co-doped LZO NPs excited by a 980 nm laser. Here, NIR photons are absorbed by the Yb³⁺ ions, followed by an ET to populate the H₅₅, F₄₅ (F₄₅) and G₄̂ avalanche levels of Tm³⁺ [32]. The D₂ level of Tm³⁺, however, is populated through cross-relaxation F₄₅ → H₅₅ : F₄₅ + D₂ (TM³⁺). It can not be directly populated through the ET of F₂⁰ / F₂⁰ (Yb³⁺) : G₄̂ → D₂ (TM³⁺) because of the large energy mismatch (around 3500 cm⁻¹) [65]. After that, the energy transfer Y₂⁰ → F₂⁰ (Yb³⁺) : D₂ → P₂₀₄ (TM³⁺) populates the P₂₀₄ (TM³⁺) levels, which then it decays nonradiatively to 1₁₆ and P₀₂ (TM³⁺) levels [66]. This is
followed by the blue radiative emission from Tm$^{3+}$ ion due to blue ($^1D_2 \rightarrow ^3F_4$ and $^1G_4 \rightarrow ^3H_6$) and UV ($^1I_{6/3}P_0 \rightarrow ^3H_6$, $^1I_{6/3}P_0 \rightarrow ^3F_4$, and $^1D_2 \rightarrow ^3H_6$) transitions.

Unlike Yb$^{3+}$ ions, Gd$^{3+}$ ions can not directly absorb 980 nm photons due to the large energy bandgap between its ground state and the first excited state. Apparently in the tridoped LZO NPs with Tm$^{3+}$, Gd$^{3+}$, and Yb$^{3+}$ ions, the energy transfer $^3P_{2,1} \rightarrow ^3H_6$ (Tm$^{3+}$) : $^8S_{7/2} \rightarrow ^6I_{1}$ (Gd$^{3+}$) populates the excited $^8I_j$ states of Gd$^{3+}$. Given that the
probability of nonradiative transition from $^6I_{7/2}$ level to the $^6P_{5/2}$ level in Gd$^{3+}$ is 5 times that of $^6I_{7/2} \rightarrow ^8S_{7/2}$ radiative transition, the non-radiative decay $^6I_J \rightarrow ^6P_J$ results in $^6P_J \rightarrow ^8S_{7/2}$ emissions \[67\]. So Gd$^{3+}$ emission was detected when the excited states $^6I_J$ and/or $^6P_J$ radiatively depopulate to the ground state. We can conclude based on above discussion that the population of the $^3P_{1,2}$ levels is important for strong UVUC from the LZO:20%Yb,1%Tm,20%Gd NPs.

The UV UC laser power dependence spectra display gradual increase...
of emission intensity with increasing laser power (Fig. 6a). Moreover, the log(f) vs log(P) plots (Fig. 6b) exhibit linear dependency with slopes of approximately 4.69, 4.80, and 4.76 for the 306, 300, and 296 nm emissions, respectively, indicating five-photon processes, similar to those reported for other phosphor systems [31,32].

4. Conclusion

In this work, LZO NPs were doubly doped with 3%Er3+ and y%Yb3+ for visible upconversion and NIR-B downconversion processes using a molten salt synthesis method. The effect of Yb3+ doping level was investigated on the UC and DC intensity of the LZO:3%Er:y%Yb NPs. As the concentration of Yb3+ dopant was increased, the orderliness degree of the pyrochlore phase and the particle size decreased. Similarly, triple doping of the LZO NPs with 20%Yb, 1%Tm, and 20%Gd was used to explore for ultraviolet upconversion. Power dependence emission intensity revealed that the VUC proceeds by 2-photon absorption whereas the UVUC via 5-photon absorption. The mechanisms of these three photoluminescence operations were explained in detail for various design strategies to improve the upconversion efficiency to make such materials more practical to be commercialized.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlumin.2019.116591.

References
