Emissions of Er^{3+} and Yb^{3+} co-doped SrZrO_3 nanocrystals under near-infrared and near-ultraviolet excitations

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Abstract: In this study, the upconversion (UC) emissions of Er^{3+} and Yb^{3+} co-doped SrZrO_3 nanocrystals (NCs) were investigated in terms of the thermal annealing temperature and concentration of Er^{3+} ions and compared with the emissions under a near-ultraviolet (near-UV) excitation. The NCs were synthesized by the combustion method, and the as-synthesized NCs were post-annealed at high temperatures. The X-ray diffraction patterns revealed that the grain sizes and crystallinity degrees of the samples increased with increasing annealing temperatures. The photoluminescence spectra of our samples exhibited strong green and very weak red emissions with the near-UV excitation, originating from the f–f transitions in the Er^{3+} ions. Interestingly, under near-infrared (near-IR) excitation, we identified sizable visible emissions at 525, 547, and 660 nm in our NCs, which indicated that the UC process successfully occurred in our NCs. These UC emissions were maximized in the NCs with an Er^{3+} concentration of 0.02 and thermal annealing at 1000 °C. We found that the intensity ratios of red to green emissions increased with increasing annealing temperatures. We discussed the differences in the emissions between near-UV and near-IR excitations.

Keywords: Er^{3+} and Yb^{3+} co-doped SrZrO_3 ; upconversion; downshifting; nanocrystals; combustion method; annealing temperature

1 Introduction

Upconversion (UC) phosphors have attracted considerable attention from researchers because of their various possible applications, such as flat panel display, solid-state laser, and bioimaging. UC is a nonlinear anti-Stokes optical process, where two or more photons are sequentially absorbed and light at a shorter wavelength than the excitation wavelength is emitted [1,2]. Most

UC materials are based on the f–f transitions of trivalent rare-earth dopants, which often show rich luminescence spectra consisting of a large number of distinct transition lines. As a representative RE element for the UC process, Er^{3+} has been known to show green and red UC emissions [3–6]. Importantly, Er^{3+} ions have several metastable high-energy levels, which give rise to transitions at various wavelengths from the infrared (IR) to the ultraviolet (UV) regions [7,8]. To improve the UC intensity of Er^{3+} , Yb^{3+} ions, with a large absorption cross section at around 980 nm, have been used as sensitizers [9,10]. Various phosphors combining the UC properties of Er^{3+} and Yb^{3+} ions have been intensively studied [11–15].

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The $4d^0$ band insulator perovskite SrZrO_3 has attracted considerable attention as a novel electronic material owing to its good high-temperature properties with thermal/chemical stability [9,10], ionic conduction, and resistivity switching behavior [11]. Recently, the SrZrO_3 compound has been found to have a good emission property [16] for applications, such as optical thermometry and bioimaging technology [17–19]. Although the emission properties of the rare-earth ion-doped SZO under the UV photoexcitation, i.e., downshifting (DS) emission, have been intensively studied [20–22], there has been no report on the UC emission property of Er^{3+} in SrZrO_3 under the near-IR photoexcitation. Because the phonon energies of SrZrO_3 are comparable to those of present UC emission hosts (WO_3 and NaYF_4) [23,24], it is worthwhile to examine the UC emissions of the SrZrO_3 compound to search for a new candidate for commercial applications.

Motivated by these considerations, we synthesized and investigated Er^{3+} and Yb^{3+} co-doped SZO NCs. The spatial confinement in NCs usually makes the electron–hole recombination easier. Indeed, there have been several reports that the intensity of the emissions is bigger in the form of nanocrystals (NCs) than in the form of bulk [25–27]. In this study, we focused on the effect of the thermal post-annealing temperature (T_{anneal}) and concentration of Er^{3+} ions on the UC emissions of SrZrO_3 NCs. Quite bright UC emissions were observed from the Er^{3+} and Yb^{3+} co-doped SZO NCs. When T_{anneal} increased, the intensity of the UC emissions and the relative intensity ratio of the red to green emissions in Er^{3+} ions also increased.

2 Experimental

2.1 Sample preparation

The Er^{3+} and Yb^{3+} co-doped SrZrO_3 (SZO:Er,Yb) NCs were prepared through the combustion method. We used $\text{Sr}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$, $\text{Er}(\text{NO}_3)_3$, and $\text{Yb}(\text{NO}_3)_3$ as raw materials and the glycine $\text{NH}_2\text{—CH—COOH}$ as a fuel. We stoichiometrically weighed $\text{Sr}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$, $\text{Er}(\text{NO}_3)_3$, and $\text{Yb}(\text{NO}_3)_3$ in a $(0.95 - x):1:x:0.05$ ratio, where $x = 0.005, 0.01, 0.02, 0.03$, and 0.05 . These components were mixed in distilled water and then dried at 100°C for 12 h. After drying, the samples were sintered at 600°C for 2 h and then finally annealed at different temperatures ($T_{\text{anneal}} = 600, 800,$

1000 , and 1200°C) for 2 h. From the infrared spectroscopy, we confirmed the absence of OH groups even for the samples annealed at 600 and 800°C .

2.2 Analysis methods

To analyze the structures of the NC samples, we measured X-ray diffraction (XRD) patterns using a Bruker-AXS D8 Discover system with a Cu target X-ray tube. The X-ray wavelength from the Cu $K\alpha$ line is $1.5418\text{ \AA}$. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained by ZEISS GeminiSEM 300 and JEM-3010 (JEOL), respectively. For the analysis of the optical properties, we measured the photoluminescence (PL) and photoluminescence excitation (PLE) spectra by a JASCO FP-8500 spectrofluorometer equipped with a xenon lamp as the source of excitation. Using a 980 nm laser diode as an IR excitation source, we measured the UC emissions of our samples with a grating-type monochromator and a photomultiplier tube detector. Samples in powder forms were used for all the measurements presented in the paper.

3 Results and discussion

3.1 Structural analysis of SZO:Er,Yb NCs

For the structural analysis, we measured the XRD patterns of our NCs. Figures 1(a) and 1(b) show the XRD patterns of $x = 0.005$ and 0.01 NCs annealed at different temperatures from 600 to 1200°C , respectively. The XRD data of the NCs annealed at $T_{\text{anneal}} = 600$ and 800°C included the phases of SrCO_3 (star symbol) and ZrO_2 (circle symbol), in addition to the main pattern of the host SZO (JCPDS 44-0161). These secondary peaks were barely identified in the NCs annealed at $T_{\text{anneal}} = 1000$ and 1200°C . We found that the XRD pattern did not change substantially with the concentration of Er^{3+} . One expects that the size mismatch between Sr^{2+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ ions ($\sim 10\%$) can lead to the decrease in the lattice constants of our samples compared with those of the undoped samples. In contrast to this expectation, we did not observe the sizable shift of the XRD peaks during the increasing of the doping concentration of Er^{3+} ions. Such incidence might be attributed to the cation size mismatch that was compensated by the cation vacancies, which were inevitable for the charge imbalance.

Fig. 1 X-ray diffraction (θ - 2θ) scans for (a) $x = 0.005$ and (b) $x = 0.01$ SZO:Er,Yb NCs annealed at T_{anneal} ($T_{\text{anneal}} = 600, 800, 1000, \text{ and } 1200\text{ }^{\circ}\text{C}$). The main peaks are indexed to the pseudo-cubic structure of SrZrO_3 (JCPDS 44-0161). The star and circle symbols indicate the peaks of SrCO_3 and ZrO_2 , respectively.

Of note, the XRD peaks showed strong T_{anneal} dependence. We estimated the (002) peak intensity and full width at half maximum (FWHM) near $2\theta = 30^{\circ}$ with T_{anneal} for the various concentrations of SZO:Er,Yb NCs. To estimate the FWHM of (002) peak for the Scherrer formula, we used the Lorentzian mode, which has been often used for the XRD analysis. With the multiple-peak fitting, we ruled out the effects of secondary phases, e.g., (111) peak of ZrO_2 , on the FWHMs of the (002) peaks. We found that the peak intensities for all concentrations of NCs gradually increased with increasing T_{anneal} , which implied that the crystallinity of our NCs was enhanced at higher T_{anneal} . At the same time, the FWHM of the (002) peak in the XRD pattern became narrower, which was directly linked to the increase of grain size [28]. We estimated the grain sizes (D) of NCs from the XRD pattern using the Scherrer formula:

$$D = \frac{0.9\lambda}{L\cos\theta} \quad (1)$$

where $\lambda = 1.5418\text{ \AA}$, θ is the Bragg angle, and L is the FWHM of the diffraction peak [29]. The grain sizes estimated from the XRD peak (002) showed strong T_{anneal} dependence: D gradually increased from 15 to 35 nm similar with all concentrations of NCs with the increasing T_{anneal} . The results on the grain sizes of SZO:Er,Yb NCs are summarized in Table 1.

Figures 2(a) and 2(b) show the SEM of the $x = 0.01$ NCs annealed at 1000 and 1200 $^{\circ}\text{C}$, respectively. In the SEM images, several cracks and voids were formed by the escaping gases during the combustion synthesis. Figures 2(c) and 2(d) show the TEM images of the $x = 0.01$ NCs annealed at 1000 and 1200 $^{\circ}\text{C}$. In the TEM images, the average grain sizes of particles were estimated as 30–40 nm. These values were a little greater than the values that we calculated from the Scherrer formula with the XRD peaks. This difference might arise from the non-monodisperse size distribution of our NCs. The change in the shapes of the NCs with T_{anneal} was found to be difficult to identify from the SEM and TEM images, mainly owing to the aggregation of the NCs.

We measured the energy-dispersive X-ray spectroscopy (EDS) to identify the elements of our NCs. Figures 3(a) and 3(b) show the EDS mapping images of the $x = 0.01$ NCs annealed at 1000 and 1200 $^{\circ}\text{C}$, respectively. The Er^{3+} and Yb^{3+} ions were uniformly distributed throughout the NCs. This finding demonstrates that Er^{3+} and Yb^{3+} ions have successfully doped into the lattices of the host. We also characterized the chemical composition of these compounds. The atomic ratio of Sr, Zr, Er, and Yb elements was about $\text{Sr:Zr:Er:Yb} = (46.1 \pm 4.8):(51.8 \pm 5.1):(0.3 \pm 0.2):(1.8 \pm 0.4)$, which was close to the nominal composition.

Table 1 Summary on the grain sizes from the XRD (002) peaks of the $x = 0.005, 0.01, 0.02, 0.03, \text{ and } 0.05$ NCs annealed at 600, 800, 1000, and 1200 $^{\circ}\text{C}$, calculated by the Scherrer formula

		Annealing temperature (°C)			
		600	800	1000	1200
Grain size (nm)	x=0.005	14.5±0.5	18.5±0.3	21.74±0.4	35.3±0.5
	x=0.01	17.2±0.5	21.0±0.3	28.2±0.4	37.0±0.5
	x=0.02	15.8±0.5	21.2±0.3	27.5±0.4	34.6±0.5
	x=0.03	14.5±0.5	17.4±0.3	21.7±0.4	35.7±0.5
	x=0.05	14.5±0.5	17.5±0.3	25.3±0.4	31.8±0.5

Fig. 2 FE-SEM images of the $x = 0.01$ NCs annealed at (a) 1000 °C and (b) 1200 °C and HR-TEM images of the $x = 0.01$ NCs annealed at (c) 1000 °C and (d) 1200 °C.

Fig. 3 Energy-dispersive X-ray spectroscopy mapping of $x = 0.01$ NCs annealed at (a) 1000 °C and (b) 1200 °C.

3.2 Downshifting in SZO:Er,Yb NCs under the near-UV excitation

3.2.1 Excitation spectra of SZO:Er,Yb NCs

Figure 4(a) shows the PLE spectra of $x = 0.02$ NCs annealed at various T_{anneal} , measured by monitoring the emissions at $\lambda_{\text{em}} = 541$ nm. We observed sharp peaks at 366 and 380 nm, which were assigned to the transitions from ground state $^4I_{15/2}$ to the excited state $^4G_{11/2}$ and $^4G_{9/2}$ in Er^{3+} , respectively [30]. Interestingly, the PLE spectra of the SZO:Er,Yb NCs strongly depended on T_{anneal} . The PLE intensities gradually increased with the increasing T_{anneal} . This behavior was

also observed with the other Er^{3+} concentrations of NCs.

We investigated the Er^{3+} concentration dependence of the PLE spectra for SZO:Er,Yb NCs ($x = 0.005$ – 0.05) annealed at $T_{\text{anneal}} = 1200$ °C. As shown in Fig. 4(b), the PLE intensity of the NCs increased with the increasing concentration of Er^{3+} up to 0.02 and then decreased above $x = 0.02$, indicative of the maximum PLE intensity at $x = 0.02$.

3.2.2 Emission spectra of SZO:Er,Yb NCs

We measured the PL spectra of our NCs under photoexcitation at $\lambda_{\text{ex}} = 380$ nm. First, we discuss the dependence of the PL spectra on T_{anneal} . Figure 5(a)

Fig. 4 (a) PLE spectra of the $x = 0.02$ NCs annealed at T_{anneal} ($T_{\text{anneal}} = 600, 800, 1000,$ and 1200 °C) and (b) PLE spectra of the $x = 0.005, 0.01, 0.02, 0.03,$ and 0.05 NCs annealed at 1200 °C, obtained by monitoring the emissions at $\lambda_{\text{em}} = 541$ nm.

Fig. 5 (a) PL spectra of the $x = 0.02$ NCs annealed at T_{anneal} ($T_{\text{anneal}} = 600, 800, 1000,$ and 1200 °C) under the $\lambda_{\text{ex}} = 380$ nm photoexcitation. (b) Emission intensities at 525 and 547 nm of $x = 0.02$ NCs as a function of the annealing temperature (T_{anneal}).

shows the PL spectra of the $x = 0.02$ NCs annealed at various T_{anneal} . We observed two strong green emission peaks at 525 and 547 nm and a weak red emission at 660 nm. The two green emissions were assigned to the transitions of $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and the red emission to the transition of $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ in Er^{3+} ions [31,32]. The fine structures, i.e., Stark splitting, in the two green emissions originated from the crystal field.

Figure 5(b) shows the intensities of the two green emissions as a function of T_{anneal} . We can identify that the intensities of emissions increased with a higher T_{anneal} , which implied that high-temperature annealing is helpful for increasing the emissions of Er^{3+} . The thermal energy from the post-annealing can help the Er^{3+} ions to diffuse well into the host material and keep the Er^{3+} ions apart from one another, avoiding the aggregation of the activators [33]. This mechanism is likely related to the reduction of the cross relaxation between Er^{3+} ions. In addition, as shown in the XRD

data, the high-temperature annealing led to the good crystallization of NCs, probably suppressing the non-radiative centers. However, the surfaces in NCs might be susceptible to the formation of the defects at high temperatures. The defects formed by the high-temperature annealing can play a role as non-radiative centers and decrease the emission intensities. Owing to the competing effects in the high-temperature annealing, the PL intensities appeared to be rather saturated above $T_{\text{anneal}} = 1000$ °C, implying that the emission intensity might be maximized just above $T_{\text{anneal}} = 1200$ °C.

Next, we discuss the dependence of the PL spectra on the concentration of Er^{3+} . Figure 6(a) shows the PL spectra of SZO:Er,Yb NCs ($x = 0.005\text{--}0.05$) annealed at $T_{\text{anneal}} = 1200$ °C. All the measured samples exhibited two strong green emissions at 525 and 547 nm and a weak red emission at 660 nm. Although no evident shift was observed for the emission peaks, the PL intensity changed with the doping concentration.

Fig. 6 (a) PL spectra of the $x = 0.005, 0.01, 0.02, 0.03$, and 0.05 NCs annealed at $1200\text{ }^{\circ}\text{C}$ under the $\lambda_{\text{ex}} = 380\text{ nm}$ photoexcitation. (b) Emission intensities at 525 and 547 nm of the NCs annealed at $1200\text{ }^{\circ}\text{C}$ as a function of the Er^{3+} concentration.

For clarity, we plotted the PL intensities of our NCs as a function of the Er^{3+} concentration in Fig. 6(b). We found that the PL intensity of the NCs increased with the increasing concentration of Er^{3+} up to 0.02 and then decreased above $x = 0.02$. This behavior indicated that the concentration quenching of Er^{3+} ions occurred at $x = 0.02$ owing to the cross relaxation, i.e., ${}^4\text{I}_{15/2} + {}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{13/2} + {}^4\text{I}_{9/2}$ [33–37].

To investigate the concentration quenching mechanism, the critical distance (R_c) of Er^{3+} ions in SrZrO_3 was calculated in accordance with Blasse's equation [38–40]:

$$R_c = 2 \left(\frac{3V}{4\pi xZ} \right)^{1/3} \quad (2)$$

where R_c is the critical distance, V is the volume of the unit cell, x is the critical concentration of Er^{3+} ions, and Z is the number of lattice sites in the unit cell that can be occupied by activator ions. For the SZO NCs

annealed at $1200\text{ }^{\circ}\text{C}$, $V = 275.98\text{ }\text{\AA}^3$, $Z = 2$, and the critical concentration of Er^{3+} was 0.02 . R_c was estimated to be $23.6\text{ }\text{\AA}$ ($> 5\text{ }\text{\AA}$) for $\text{Er}^{3+}\text{--}\text{Er}^{3+}$. This finding suggests that the multipolar interaction mechanism should be associated with the energy transfer between Er^{3+} and Er^{3+} .

3.3 Upconversion emission of SZO:Er,Yb NCs under the near-IR excitation

3.3.1 UC emission of SZO:Er,Yb NCs

We investigated the UC emission spectra of SZO:Er,Yb NCs under 980 nm diode laser excitation at room temperature and found that the UC emissions were successfully achieved in SZO:Er,Yb NCs. Figure 7(a) shows the UC emission spectra of $x = 0.01$ NCs annealed at various T_{anneal} . We identified two distinct green emissions at 525 and 547 nm and one red emission at 660 nm , which are assigned to ${}^2\text{H}_{11/2} \rightarrow$

Fig. 7 (a) UC emission spectra of the $x = 0.01$ NCs annealed at T_{anneal} ($T_{\text{anneal}} = 600, 800, 1000$, and $1200\text{ }^{\circ}\text{C}$) under the $\lambda_{\text{ex}} = 980\text{ nm}$ photoexcitation. (b) Emission intensities at $525, 547$, and 660 nm of $x = 0.01$ NCs as a function of the annealing temperature (T_{anneal}).

$^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$, respectively. The Stark splitting was not identified in the UC spectra owing to the low spectral resolution in our UC spectrometer. The intensity of the UC emissions increased with increasing T_{anneal} up to 1000 °C and then decreased for $T_{\text{anneal}} = 1200$ °C. For clarity, we plotted the emission intensities of the three peaks as a function of T_{anneal} in Fig. 7(b). Clearly, the UC luminescence intensities were maximized at $T_{\text{anneal}} = 1000$ °C. Generally, the high-temperature annealing leads to good crystallization, which consequently increases the emission intensity [41,42]. Our samples had better crystallization and bigger grain size when the samples were annealed at high temperatures than at low temperatures. Here, we need to consider another effect of defects. The defects within the samples should increase with the increasing T_{anneal} , but it was hard to estimate the amount of the defects. In this sense, the NCs for $T_{\text{anneal}} = 1000$ °C were highly likely to have less defects than those for $T_{\text{anneal}} = 1200$ °C. We speculated that the two competing effects, i.e., defect and crystallization, account for the quenching of the UC emissions at 1000 °C. For low-temperature annealing below 1000 °C, the positive effect of crystallization was dominant, whereas for high-temperature annealing above 1200 °C, the negative effect of defects was dominant.

Figure 8(a) shows the UC emission spectra of SZO:Er,Yb NCs ($x = 0.005$ – 0.05) annealed at $T_{\text{anneal}} = 1000$ °C. Two strong green and one red emissions were observed, and evident shifts of the emissions were not detected. To clarify the evolution of UC spectra with the Er^{3+} concentration, we plotted the intensities of the UC three peaks as a function of the Er^{3+} concentration

in Fig. 8(b). The Er^{3+} ions were clearly quenched at $x = 0.01$, which was smaller than $x = 0.02$ for the DS emission, as discussed in Section 3.2.2. Accordingly, in the UC process, the cross relaxation should be associated with the energy transfer between Er^{3+} and Yb^{3+} ions rather than between the Er^{3+} ions. This difference indicated that the energy transfer from Yb^{3+} to Er^{3+} plays a crucial role in obtaining the UC emissions in SZO:Er,Yb NCs.

We also calculated the critical distance between Er^{3+} and Yb^{3+} using Eq. (2). We used $V = 275.98 \text{ \AA}^3$, $Z = 2$, and $x = 0.06$ from the total concentrations of Er^{3+} and Yb^{3+} . R_c was estimated to be $16.4 \text{ \AA}$ for Er^{3+} – Yb^{3+} , so the energy transfer between Er^{3+} and Yb^{3+} was considered to be associated with the multipolar interaction mechanism.

Another interesting point is the change in the relative intensity of the green and red UC emissions. The inset of Fig. 8(b) presents the intensity ratios of the 660–525 nm emissions. When the concentration of Er^{3+} ions increased, the intensity ratio also increased from ~ 3 at $x = 0.005$ to 5.98 at $x = 0.05$. This increase might be attributed to the cross relaxation of $^2F_{7/2} + ^4I_{11/2} \rightarrow ^2F_{9/2} + ^2F_{9/2}$, which became dominant with the increasing concentration of the Er^{3+} ions.

3.3.2 Mechanism of the UC emissions in SZO:Er,Yb NCs

Figure 9 shows an energy-level scheme for the mechanism of the UC process. In our systems, the 980 nm photoexcitation energy corresponded to a transition from the ground state $^4I_{15/2}$ to the excited state $^4I_{11/2}$ in the Er^{3+} ions. Excited electrons in the $^4I_{11/2}$ state were excited once more to a higher excited

Fig. 8 (a) UC emission spectra of the $x = 0.005, 0.01, 0.02, 0.03$, and 0.05 NCs annealed at 1200 °C under the $\lambda_{\text{ex}} = 980$ nm photoexcitation. (b) Emission intensities at 525, 547, and 660 nm of the NCs annealed at 1200 °C as a function of the Er^{3+} concentration. Inset of Fig. 8(a) is the enlarged spectra in the range of 523–530 nm and inset of Fig. 8(b) is the intensity ratios of the 660 nm to 525 nm emissions as a function of the Er^{3+} concentration (x).

level $^2F_{7/2}$ through the absorption of a secondary 980 nm photon, where the transition energy from $^4I_{15/2}$ to $^2F_{7/2}$ was twice that of the transition from $^4I_{15/2}$ to $^4I_{11/2}$. Some of the electrons in the $^2F_{7/2}$ state relaxed non-radiatively to $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ states. Moreover, electrons in the $^4I_{11/2}$ states relaxed non-radiatively to $^4I_{13/2}$. The electrons in $^4I_{13/2}$ were also excited to the excited $^4F_{9/2}$ state through the absorption of a secondary 980 nm photon. Then, the radiative transitions of electrons in the $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ states to the ground state $^4I_{15/2}$ led to the emissions at 525, 547, and 660 nm, respectively [43,44]. When the Er^{3+} concentration reached a certain degree, the cross-relaxation process $^4I_{15/2} + ^2H_{11/2} \rightarrow ^4I_{13/2} + ^4I_{9/2}$ and $^2F_{7/2} + ^4I_{11/2} \rightarrow ^2F_{9/2} + ^2F_{7/2}$ took place. Here, the Yb^{3+} ions assisted the UC process through the energy transfer. The Yb^{3+} ions had a 980 nm energy gap between the $^2F_{5/2}$ and $^2F_{7/2}$ states, with a large absorption cross section. The absorbed 980 nm photon energy was transferred to the neighboring Er^{3+} ions, which promoted the upward transitions of $^4I_{15/2} \rightarrow ^4I_{11/2}$, $^4I_{13/2} \rightarrow ^4F_{9/2}$, and $^4I_{11/2} \rightarrow ^2F_{7/2}$ in Er^{3+} [45]. The energy transfer efficiency from Yb^{3+} to Er^{3+} could be calculated from the Yb^{3+} doping dependence of the Er^{3+}/Yb^{3+} emissions. Here, the back energy transfer from Er^{3+} to Yb^{3+} may occur, although it is relatively smaller than the energy transfer from Yb^{3+} to Er^{3+} . To address this issue, the emissions of Er^{3+} and Yb^{3+} need to be compared carefully in the intensity and decay process.

The red emission was dominant over the green emissions in the UC process, and it was the opposite in the DS process. The values of the red to green emissions were estimated to be 3.078–5.982 and 0.024–0.075 in the UC and DS emission spectra, respectively. The dominance of the green emissions over the red emissions indicated that the relaxation time of $^2H_{11/2}$ and $^4S_{3/2}$ to $^4I_{15/2}$ should be much shorter than that of $^4F_{9/2}$. In this sense, the DS process to excite electrons to a higher energy level than $^2H_{11/2}$ and $^4S_{3/2}$ cannot be useful in contributing to the red emissions from $^4F_{9/2}$. The dominance of the red emissions over the green emissions in the UC emission spectra suggested that the transitions of $^4I_{15/2} \rightarrow ^4I_{11/2} \rightarrow ^4I_{13/2} \rightarrow ^4F_{9/2}$ (thick lines in Fig. 9) are most effective in the UC process in SZO:Er,Yb NCs.

3.3.3 Power dependence of the UC emission in SZO:Er,Yb

We investigated the excitation power dependence of

Fig. 9 Energy-level schemes of Er^{3+} and Yb^{3+} and optical transitions: photoexcitations (upward arrows), radiative relaxations (downward solid arrows), non-radiative relaxations (downward dotted arrows), cross relaxations (gray dotted line), and energy transfers from Yb^{3+} to Er^{3+} (curved lines).

the UC emissions of SZO:Er,Yb NCs to identify the number of absorbed electrons for the UC process. The UC luminescence intensity (I) is related to the excitation power (P) through the following formula [45,46]:

$$I \propto P^n \quad (3)$$

where I is the emission intensity of the UC luminescence and P is the average excitation power of the 980 nm laser. n corresponds to the number of the required excitation photons from the ground state to the emitting state, which can be obtained from the slope of the UC luminescence intensity with respect to the laser excitation power in the double logarithmic plot. Figure 10 shows the log–log plot of the UC emission intensity versus the excitation power for SZO:Er,Yb NCs. For all samples, the n values were close to 2, which indicated that the UC emissions of the samples should belong to two-photon UC processes.

3.4 CIE coordinates of SZO:Er,Yb NCs

We calculated the CIE chromaticity coordinates (x , y) of SZO:Er,Yb NCs of $x = 0.01$ and $x = 0.02$ for the DS and UC. Owing to the difference in the relative intensity of the red to the green emissions, the CIE coordinates showed a sharp contrast between the DS and UC emissions in Fig. 11. The dominance of the green emission in the DS spectra accounted for the closeness to the blue color of our samples. On the other hand, the dominance of the red emission in the UC

Fig. 10 Excitation power dependence of the two green and one red emissions in (a) $x = 0.005$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$, and (e) $x = 0.05$, annealed at 1200 °C.

spectra was responsible for the closeness to the red color of the samples. The DS and UC emissions had a common tendency where the color of NCs shifted to green with increasing T_{anneal} for all concentrations. By combining the emissions in the DS and UC processes, we can tune the emission property of the SZO:Er,Yb phosphor in a wide range of colors.

4 Conclusions

We investigated the emission properties of Er^{3+} and Yb^{3+} ion doped SZO NCs synthesized by the combustion method with post-thermal annealing under near-UV

Fig. 11 CIE chromaticity diagram of SZO:Er,Yb NCs for (a) DS and (b) UC.

and near-IR excitations. The XRD patterns revealed that with increasing annealing temperature, the grain sizes and crystallinity degrees of the NCs increased for all Er^{3+} concentrations. The PL spectra of our samples, originating from the f–f transitions in the Er^{3+} ions, exhibited strong green emissions with the near-UV excitation, strongly depending on the annealing temperature and Er^{3+} concentration. Under the near-IR excitation, we identified sizable visible emissions at 525, 547, and 660 nm in our NCs, which indicated that the UC process successfully occurred in our NCs. These UC emissions were maximized in the NCs with the Er^{3+} concentration of 0.02 and thermal annealing at 1000 °C. The intensity ratio of red to green emissions increased with the increasing annealing temperature. We also observed the differences in the emissions between the near-UV and near-IR excitations with respect to the critical concentration in the quenching and the relative intensity of the red emissions to the

green emission. These results suggest that the near-UV and near-IR excitations are complementary in tuning the emission properties of the SZO:Er,Yb phosphor.

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