Monodisperse hexagonal-phase Gd$_2$O$_2$S:Yb$^{3+}$,Er$^{3+}$ submicrospheres have been successfully prepared for the first time by means of a solvothermal method. The SEM and TEM results show that the spherical size is between 210–300 nm and the submicrospheres are of polycrystalline nature. Under the excitation of 980 nm, the bright green emission of the Gd$_2$O$_2$S:Er$^{3+}$ at about 524 and 548 nm are assigned to the $^2$H$_{11/2}$$rightarrow$^4$I_{15/2}$ and $^4$S$_{3/2}$$rightarrow$^4$I_{15/2}$ transitions of the Er$^{3+}$ ions, respectively. The incorporation of Yb$^{3+}$ ions into the Gd$_2$O$_2$S:Er$^{3+}$ leads to the decrease in the intensity ratio of the green luminescence to the red luminescence. The corresponding emission color can be tuned from green to yellow by varying the Yb$^{3+}$ concentration. The analysis reveals that the two-photon absorption is mainly responsible for the upconversion luminescence in Gd$_2$O$_2$S:Yb$^{3+}$,Er$^{3+}$ submicrospheres.

1. Introduction

Since its discovery in the 1960s, upconversion (UC) materials containing rare earth ions have been the focus of much research.\textsuperscript{1} Along with the progress of science and nanotechnology, UC nanocrystals have received much attention owing to their wide potential applications in such fields as infrared detection, molecule recognition, three-dimensional displays, and especially luminescent probes in biological labeling and imaging technology.\textsuperscript{2} Up to now, various upconversion materials have been developed and studied, most of the work is focused on the investigation of halides, glass, and oxides.\textsuperscript{3} It is well-known that host materials with low phonon energies (ho) show high upconversion luminescence efficiency by suppressing the non-radiative multiphonon relaxation. Usually, ho$_{\text{fluoride}}$< ho$_{\text{aluminate}}$, so most efficient upconversion luminescence has been realized in fluoride hosts. Many micro-/nano scale fluorides upconversion materials have been reported, such as, NaYF$_4$:Yb$^{3+}$,Er$^{3+}$,\textsuperscript{4} BaYF$_5$:Yb$^{3+}$,Er$^{3+}$,(Tm$^{3+}$),\textsuperscript{5} and LaF$_3$:Yb$^{3+}$,Er$^{3+}$ (Tm$^{3+}$, Ho$^{3+}$).\textsuperscript{6} However, these materials usually present poor mechanical properties, moisture sensitivity, and non-eco-friendly. Most of the oxides are chemical stable and nontoxic, are also widely reported as candidates of upconversion materials,\textsuperscript{7} but they show low upconversion luminescence efficiency. Rare-earth oxysulfides possess favorable chemical durability, and they are eco-friendly and nontoxic. Yocom et al.\textsuperscript{8} demonstrated that Y$_2$O$_2$S:Yb$^{3+}$,Er$^{3+}$ exhibited 82% lighter output to that of fluoride. Liu et al.\textsuperscript{9} reported the anomalous thermalization effect in Er$^{3+}$ doped Y$_2$O$_2$S. So rare-earth oxysulfides may be candidates for upconversion materials.

The trivalent rare-earth (RE) ions, such as Er$^{3+}$, Tm$^{3+}$, Ho$^{3+}$, Nd$^{3+}$, Yb$^{3+}$, and Pr$^{3+}$, are suitable candidates for UC processes due to their abundant energy levels and narrow emission spectral lines. Especially the introduction of Yb$^{3+}$ ions as a sensitizing center with a pumping wavelength of around 1 μm, for which high-power sources are commercially available, has allowed a large enhancement of the UC luminescence of the activators Tm$^{3+}$, Er$^{3+}$, and Ho$^{3+}$.

Gd$_2$O$_2$S nanocrystals doped with RE$^{3+}$ ions have particularly attracted considerable interest in terms of high chemical durability and thermal stability. A number of different techniques have been developed to synthesize nanocrystals, such as the thermal decomposition method and conversion of the Gd(OH)$_3$ method.\textsuperscript{11} So far, the investigations for RE$^{3+}$-doped Gd$_2$O$_2$S nanocrystals have mostly concentrated on downconversion luminescence such as Eu$^{3+}$- and Tb$^{3+}$-doped Gd$_2$O$_2$S nanocrystals. But little is reported on the upconversion luminescence of Gd$_2$O$_2$S nanocrystals. On the other hand, it is well-known that the oxysulfides have low phonon energies, low symmetry, favorable chemical stability and nontoxicity.\textsuperscript{12} Thus, Gd$_2$O$_2$S is an ideal host for the design of upconverting phosphors. In 2004, Hirai and Orikoshi\textsuperscript{13} reported upconverting phosphor Gd$_2$O$_2$S:Yb,Er particles synthesized by an emulsion liquid membrane method. Under 980 nm laser excitation, Gd$_2$O$_2$S:Yb,Er particles exhibited green emission. In 2007, Hu et al.\textsuperscript{14} reported an upconversion afterglow phenomenon of Er$^{3+}$ in Gd$_{1.93}$O$_2$S:0.01Er,0.03Yb,0.02Ti,0.01Mg phosphor. In addition, with the codoping of Ti$^{4+}$ and Mg$^{2+}$ ions, the unusual phosphorescence was improved. Although the upconversion emission for Gd$_2$O$_2$S:Yb,Er has been reported, the effect of Yb$^{3+}$ concentration on the upconversion properties has not been discussed in detail. In this paper, we report the preparation and
UCL properties of Gd$_2$O$_2$S:Yb$^{3+}$/Er$^{3+}$ monodisperse submicrospheres, especially the influence of Yb$^{3+}$ codoping on UCL process of Er$^{3+}$ ions.

2. Experimental section

2.1 Materials

The initial chemicals, including Gd$_2$O$_3$, Yb$_2$O$_3$, and Er$_2$O$_3$ (all with purity = 99.99%, Shanghai Yuelong Non-Ferrous Metals Limited., China), HNO$_3$, ethylene glycol, poly(vinyl pyrrolidone) (PVP K30, M = 40 000), thiourea, and ethanol (all with purity of A.R., Beijing Fine Chemical Company, China), were used without further purification. Rare-earth nitrate stock solutions were prepared by dissolving the corresponding metal oxide in nitric acid at elevated temperatures.

2.2 Preparation

In a typical procedure, appropriate amounts of Gd(NO$_3$)$_3$ (1 M), Yb(NO$_3$)$_3$ (0.5 M), and Er(NO$_3$)$_3$ (0.05 M) were added into 25 mL of ethylene glycol. 2.0 g PVP was added into the above solution. After vigorous stirring for 10 min, the PVP was dissolved thoroughly. Then 10 mL of ethanol solution containing 0.11 g thiourea was added dropwise into the above solution. The as-obtained solution was stirred for another 30 min. The resulting transparent feedstock was transferred to a 50 mL Teflon-lined stainless autoclave and heated at 200°C for 24 h. After naturally cooling to room-temperature, the precursors were separated by filtration, washed with ethanol and deionized water several times, and dried in atmosphere at 60°C over night. The final products were obtained through a heat treatment at 700°C for 2 h under N$_2$/S atmosphere.

2.3 Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 focus X-ray powder diffractometer with Cu-Kα radiation (λ = 0.15405 nm). The size and morphology of the samples were inspected using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan). The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns were obtained by a JEOL-2010 transmission electron microscope at an accelerating voltage of 200 kV. The UC emission spectra were obtained by using a 980 nm laser diode Module (K98D08M-30W, China) as the excitation source and detected by an R955 instrument (hama-matsu) from 400 to 900 nm. All the measurements were performed at room temperature.

3. Results and discussion

3.1 Structure and morphology

Fig. 1 shows the XRD patterns of the precursor and Gd$_2$O$_2$S:Yb,Er submicrospheres. There are two broad peaks near 2θ = 28.55° and 47.26° for the precursor, indicating that the precursor is composed of amorphous gadolinium compound. After being annealed at 700°C for 2 h in N$_2$/S atmosphere, all diffraction peaks can be readily indexed to the pure hexagonal phase of Gd$_2$O$_2$S (space group: P3m1(164)) according to the JCPDS file no. 26-1422. No additional peaks of other phases have been found, indicating that the Yb$^{3+}$ and Er$^{3+}$ ions are effectively built into the host lattice.

SEM and TEM are used to characterize the morphology and crystal structure of the products. Fig. 2(a) and (b) show typical SEM images of the precursor and the final product. The precursors consist of homogeneous and monodisperse spheres with diameters 240–330 nm. After being annealed at 700°C, the obtained Gd$_2$O$_2$S:1%Er inherits the spherical shape from the precursor. But their average diameter is reduced to 210–300 nm because of the decomposition of the precursor. A typical TEM image and selected area electron diffraction (SAED) pattern for the Gd$_2$O$_2$S:1%Er$^{3+}$ (Fig. 2(c) and 2(d)) clearly confirm that the diameter of the Gd$_2$O$_2$S:1%Er$^{3+}$ submicrospheres is about 210–300 nm and the spheres actually further consist of small grains, consistent with the value shown in the SEM images. The SAED image contains partial ring and dot patterns, indicating that the Gd$_2$O$_2$S:1%Er$^{3+}$ submicrospheres are of polycrystalline nature.

3.2 Upconversion luminescence properties

Fig. 3 shows the room-temperature upconversion fluorescence spectra of the Gd$_2$O$_2$S:Yb$^{3+}$,Er$^{3+}$ submicrospheres with different contents of Yb$^{3+}$ ions. Under 980 nm NIR excitation, the
Gd$_2$O$_2$S:1%Er$^{3+}$ exhibits bright green emission. Two primary bands at about 524 and 548 nm are assigned to the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions of the Er$^{3+}$ ions, respectively. A weak band at about 671 nm is ascribed to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition of the Er$^{3+}$ ions. However, the green emission of the Gd$_2$O$_2$S:1%Er$^{3+}$ submicrospheres changes greatly when Yb$^{3+}$ ions were doped into Gd$_2$O$_2$S:1%Er$^{3+}$. As can be seen from Fig. 3, the Gd$_2$O$_2$S:20%Yb$^{3+}$,1%Er$^{3+}$ submicrospheres show mainly red emission at about 671 nm and weak green emissions at about 524 and 548 nm of the Er$^{3+}$ ions, which can be assigned to the transitions of $^4F_{9/2} \rightarrow ^4I_{15/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$, and $^4S_{3/2} \rightarrow ^4I_{15/2}$, respectively. The 410 nm emission ($^2H_{9/2} \rightarrow ^4I_{15/2}$) is also measured, but the intensity is much weaker than that of green and red luminescence, as shown in the inset of Fig. 3. The concentration dependence upconversion spectra of Gd$_2$O$_2$S:xYb$^{3+}$,1%Er$^{3+}$ are investigated and shown in Fig. 3. With the increase of Yb$^{3+}$ concentration from 0 to 20 mol%, the green emission intensity decreases remarkably while the red emission intensity increases. Thus, it is possible to tune the emission color of the Gd$_2$O$_2$S:Yb$^{3+}$,Er$^{3+}$ submicrospheres by varying the Yb$^{3+}$ concentration.

It is well known that the UPL intensity ($I_{UPL}$) is proportional to some power $n$ of the incident excitation power ($I_p$) according to $I_{UPL} \propto I_p^n$, where superscript $n$ represents the number of pump photons required to populate the emitting states. The number of pumping photons ($n$) can be determined from the slope of the photoluminescence intensity versus the laser excitation power in a log–log plot. These plots are shown in Fig. 5 for the Gd$_2$O$_2$S:10%Yb$^{3+}$,1%Er$^{3+}$ submicrospheres. The $n$ values of Gd$_2$O$_2$S:10%Yb$^{3+}$,1%Er$^{3+}$ are calculated to be 2.25 and 2.26 for the green and red emissions, respectively. The results show that two-photon process is mainly responsible for green and red upconversion for Gd$_2$O$_2$S:10%Yb$^{3+}$,1%Er$^{3+}$ sample. The similar phenomenon was also observed in other Yb$^{3+}$/Er$^{3+}$ codoped Gd-based oxide particles, where the upconverted emissions were also two-photon process. Therefore, the upconversion mechanism of Yb$^{3+}$–Er$^{3+}$ systems in Gd$_2$O$_2$S spheres can be built according to the experimental results and the references as shown in Fig. 6.

In principle, three basic population mechanisms may be involved in the upconversion process, namely excited state absorption (ESA), energy transfer upconversion (ET), and...
the energy transfer from the excited Yb$^{3+}$ ions. The Er$^{3+}$ ions transit to the ground state and emit red light. If the excitation photon density is high enough, the electron at the $^4S_{3/2}$ level of the Er$^{3+}$ ion can absorb another photon and transit to the $^4K_{15/2}$ level. After nonradiative decay to $^2G_{11/2}$ state, electrons can populate the $^6F_{5/2}$ state by energy transfer from the excited Er$^{3+}$ ions to the ground-state Yb$^{3+}$ ions through the following process:

$$^4G_{11/2} (\text{Er}^3+) + ^2F_{7/2} (\text{Yb}^3+) \rightarrow ^4F_{9/2} (\text{Er}^3+) + ^2F_{5/2} (\text{Yb}^3+)$$

In addition, the electrons also can nonradiatively relax to the $^2H_{9/2}$ state, resulting in 410 nm luminescence, which should be responsible for the three-photon process. The fact that the red emission is enhanced with increasing Yb$^{3+}$ concentration reveals that the level $^4F_{5/2}$ was largely populated. One of the most likely reasons is that introduction of an elevated amount of Yb$^{3+}$ dopants into the Gd$_2$O$_2$S host lattice would decrease the interatomic distance between the Yb$^{3+}$ ions and Er$^{3+}$ ions and thus facilitates the back-energy-transfer process from the Er$^{3+}$ to Yb$^{3+}$ ions: $^4G_{11/2} (\text{Er}^3+) + ^2F_{5/2} (\text{Yb}^3+) \rightarrow ^4F_{9/2} (\text{Er}^3+) + ^2F_{5/2} (\text{Yb}^3+)$. The back-energy-transfer should subsequently suppress the population in excited levels of the $^4S_{3/2} (^2H_{11/2})$, resulting in the decrease of the green-light emission ($^4H_{11/2} ^2S_{3/2} \rightarrow ^4I_{15/2}$). Meanwhile, the back-energy-transfer directly populates the $^4F_{9/2} (\text{Er}^3+)$ level, producing the enhancement of red ($^2F_{2/2} \rightarrow ^4I_{15/2}$) emission. Considering the back-energy-transfer and the nonradiative relaxation processes, the required photon number of upconversion red and green emissions should be more than two, which agrees well with our experimental results.

**Conclusion**

In summary, a general approach has been developed for the synthesis of the well-disperse hexagonal Gd$_2$O$_2$S:Yb$^{3+}$,Er$^{3+}$ submicrospheres. Under the excitation of 980 nm, the red emission ($^2F_{9/2} ^4I_{15/2}$) of the Gd$_2$O$_2$S:Yb$^{3+}$/Er$^{3+}$ increases with increasing the Yb$^{3+}$ concentration, while that of the green emission ($^2H_{11/2} ^2S_{3/2} \rightarrow ^4I_{15/2}$) decreases. The red emission enhancement is attributed to the enhanced population of the $^4F_{9/2}$ level via the energy transfer ($^4G_{11/2} (\text{Er}^3+) + ^2F_{7/2} (\text{Yb}^3+) \rightarrow ^4F_{9/2} (\text{Er}^3+) + ^2F_{5/2} (\text{Yb}^3+)$), while green emission diminishment is attributed to $^4S_{3/2} + ^2F_{5/2} \rightarrow ^4K_{15/2} + ^2F_{7/2}$, which depopulates the excited $^4S_{3/2}$ level at higher Yb concentrations. So the emission color can be tuned from green to yellow only by changing the Yb$^{3+}$ concentration. We have also confirmed that the upconversion process in Gd$_2$O$_2$S:Yb$^{3+}$,Er$^{3+}$ submicrospheres results from two-photon processes. These materials may have potential applications as bio-probes and displays.

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