Bright Green Upconversion Fluorescence of Yb$^{3+}$, Er$^{3+}$-Codoped NaYF$_4$ Nanocrystals

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Uniform hexagonal NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ nanocrystals (NCs) with bright green upconversion fluorescence were prepared. The nanocrystals were highly hydrophobic and dispersed in cyclohexane forming a transparent colloidal solution due to the use of oleic acid as a capping ligand. Temperature dependence for emission of Er$^{3+}$ ions in this sample was also studied. The green emission intensity of Er$^{3+}$ ions had a maximum at 160 K under 980 nm excitation, which was attributed to the thermally activated distribution of electrons and the thermal quenching effect. The transparent colloidal solution is expected to be a good candidate for research in biological imaging or display applications.

Keywords: NaYF$_4$, Rare Earth, Nonradiative Relaxation.

1. INTRODUCTION

A number of rare-earth-doped fluoride nanocrystals and submicrocrystals with efficient infrared (IR) radiation into visible light through frequency upconversion (UC) at room temperature have been produced.\cite{1-6} Due to the low photon energy, the relatively high efficiency of the UC process in these fluoride crystals, and the inexpensive 980 nm near-IR (NIR) diode lasers, the realization of efficient NIR to visible upconverting nanocrystals and submicrocrystals should unlock a realm of new possibilities in the field of biosensors, displays, and short-wavelength lasers. It is well-known that the size and shape of inorganic nanocrystals have great influence on their physical properties.\cite{7,8} Thus, further explorations of novel nanomorphology, with controlled size and shape by convenient synthesis methods, is of great importance for the development of new functional devices. Simultaneously, in order to realize the biological imaging or display applications based on the UC principle in a fluid, it is crucial to investigate lanthanide-doped UC nanocrystalline colloidal solutions. To date, the successful preparation of transparent colloidal solutions has been demonstrated in a few NaYF$_4$ nanocrystals. However, its temperature-dependent luminescence behavior was seldom studied. In this letter, we report a study on the transparent NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ nanocrystal colloidal solution.

Under 980 nm excitation from a laser diode, the transparent solution presented bright green UC fluorescence. It is expected to be a good candidate for research in biological imaging or display applications. We also investigated the temperature-dependent characteristics of Er$^{3+}$ ion emissions. The understanding of this process is helpful in the search for high efficiency phosphors. Thermalization effects between the $^2$H$_{11/2}$ and $^4$S$_{3/2}$ levels separated by 765 cm$^{-1}$ in these fluoride nanocrystals were also reported. The results show that 520 nm emission is favored at high temperatures by its higher emission cross section and that the overall green fluorescence increases consequently.

2. EXPERIMENTAL DETAILS

In a typical preparation, 0.6 g NaOH was dissolved in a solution containing oleic acid, ethanol, and deionized water (10/5/4, v/v/v). Then 1.5 mmol KF, 0.39 mmol Y(NO$_3$)$_3$·6H$_2$O, 0.10 mmol Yb(NO$_3$)$_3$·6H$_2$O and 0.01 mmol Er(NO$_3$)$_3$·6H$_2$O were added to the solution under vigorous stirring. The mixture was agitated for 30 min and then transferred into a 50-mL autoclave, sealed, and treated at 180 °C for 16 h. Subsequently, the mixture was allowed to cool to room temperature, and the powder was obtained by centrifuging, rinsing, and drying. Phase identification was performed via X-ray diffraction (XRD, model Rigaku RU-200b), using nickel-filtered...
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Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å). The size and morphology of the nanocrystals were characterized by transmission electron microscopy (TEM, JEM, 2000EX 200 kV). High-resolution emission spectra were obtained at 13–300 K with the sample mounted in a helium exchange gas chamber of a closed cycle refrigeration system. A 980 nm laser diode was used as the excitation source. The fluorescence photo of the colloidal solution with 0.2 mg/mL concentration in cyclohexane was acquired with a digital camera under 980 nm excitation from a laser diode.

3. RESULTS AND DISCUSSION

The crystal structure and the phase purity of the material was obtained by XRD, as shown in Figure 1. According to JCPDS standard cards, the NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ nanocrystals exhibit a pure hexagonal structure. The XRD pattern also demonstrates that the Na ions can be incorporated into the framework of YF$_n$, forming NaYF$_4$.

Figure 2(a) shows the TEM image of hexagonal-phase NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ nanocrystals. The image clearly reveals that the morphology of the as-synthesized nanocrystals is hexagonal nanoplates with a mean size of 200 nm. In the image, there is no aggregation of nanocrystals, which indicates the good dispersion of this sample. In addition, these nanocrystals are highly crystalline. Their high crystallinity is also inferred from the electron diffraction images (insert in Fig. 2(a)). Figure 2(b) illustrates photographs of hexagonal-phase NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ dispersed in cyclohexane with the concentration of 2 mg/mL. We can see that the colloidal solution is fully transparent in the left picture, and the right picture shows that the colloidal solution emits eye-visible upconversion luminescence under 980 nm excitation. This solution is stable for months without any visible precipitate. The surfaces of the synthesized NaYF$_4$ nanocrystals were covered by the surfactant oleic acid, so the nanocrystals were highly hydrophobic and dispersed in cyclohexane.

The normalized UC emission spectra of hexagonal-phase NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ nanocrystals at three different temperatures under 980 nm excitation are shown in Figure 3. The laser power is 400 mW. In the spectra, the green emission peaks are observed in the range of 515–560 nm, corresponding to the $2H_{11/2} \rightarrow 4I_{15/2}$ transitions, while the red emission peaks are observed between 640 and 680, corresponding to the $4F_{9/2} \rightarrow 4I_{15/2}$ transitions. At 13 K, the $2H_{11/2}$ fluorescence intensity is negligible, and it progressively increases with increasing temperature. This is a representative behavior of processes involving the thermally coupled $4S_{3/2}$ and $2H_{11/2}$ as reported elsewhere.$^9$,$^{10}$

The upconversion luminescence mechanism and population process in Er$^{3+}$/Yb$^{3+}$-codoped systems are presented...
in Figure 4. Following 980 nm irradiation, the Er\(^{3+}\) ion is excited to the \(4F_{7/2}\) state via two successive energy transfers from the Yb\(^{3+}\) ions in the \(4I_{15/2}\) state. Thus, one Yb\(^{3+}\) ion will transfer its energy to an Er\(^{3+}\) ion in the ground state, thereby exciting it to the \(4I_{11/2}\) state. This process is followed by a transfer of energy from another Yb\(^{3+}\) ion also in its excited state, resulting in the population of the \(4F_{7/2}\) state of the erbium ion. The lower emitting levels are then populated via multiphonon relaxation, and green and red emissions are then observed. Of course, interactions between two Er\(^{3+}\) ions cannot necessarily be ignored. A near infrared (NIR) photon from the pump beam will also excite an Er\(^{3+}\) ion to its \(4I_{11/2}\) state. Another Er\(^{3+}\) ion also in the \(4I_{11/2}\) state and in close proximity will transfer its energy to the initial ion, thereby exciting it to the \(4F_{7/2}\) state. However, following the addition of Yb\(^{3+}\) ions, this process is greatly diminished due to the large absorption cross-section of the ytterbium ions. Thus, the simultaneous transfer of energy from Yb\(^{3+}\), which populates the \(4F_{7/2}\) state, is dominant.

The dependence of the upconversion efficiency upon temperature was examined, and the results are depicted in Figure 5. As can be inferred from experimental data, the visible emission efficiency increased by a factor of 4 when the sample was cooled from room temperature to 160 K. This behavior reflects the competition between the two major thermal effects acting in the system as follows. One thermal effect is the temperature-enhanced sideband anti-Stokes excitation of the sensitizer, which is responsible for the increase in the upconversion emission efficiency. The expression of the absorption cross-section related to the temperature is written as 

\[
\sigma(T) = \sigma(0)\exp\left(-\frac{\hbar\omega}{k_B T}\right) - 1 = \frac{\Delta E}{\hbar \omega},
\]

where \(\sigma(0)\) is the absorption cross section at 0 K and \(\hbar \omega\) is the photon energy. The other thermal effect is the thermally enhanced nonradiative decay rate that inhibits radiative emission. The nonradiative transition probability between levels for low concentrations of Er\(^{3+}\) ions is due to multiphonon relaxation processes, and can be related to the temperature through 

\[
W_{NR} = W_{NR}(0)\left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)\right]^{-1}.
\]

where \(W_{NR}(0)\) is the nonradiative relaxation rate at 0 K.

It can also be seen from Figure 5(b) that the green emission from \(4S_{3/2}\) decreases faster than the red emission from \(4F_{9/2}\) above 180 K as temperature increases. As mentioned above, there are two main factors. One factor is the thermal quenching effect of luminescence. The intermediate level of the green emission is \(4I_{11/2}\), while that of the red emission is \(4I_{13/2}\). For the red as well as the green emission, the nonradiative relaxation of \(4I_{11/2} \rightarrow 4I_{13/2}\) and \(4S_{3/2} \rightarrow 4F_{9/2}\) is involved, which increases the electron population on \(4F_{9/2}\) while decreasing that on \(4S_{3/2}\). That makes the red emissions decrease slower than that of green emissions. As is well known, the nonradiative relaxation probability is size-dependent. As the particle size

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**Fig. 4.** Schematic diagram of Yb\(^{3+}\)-sensitized Er\(^{3+}\) upconversion under 980 nm excitation. The solid lines represent radiative transitions, and the dashed lines represent nonradiative transitions.

**Fig. 5.** (a) Visible UC luminescence spectra in NaYF\(_4\):Yb\(^{3+}\), Er\(^{3+}\)–Codoped NaYF\(_4\) Nanocrystals at different temperatures. (b) The upconversion emission intensity of \(4S_{3/2} \rightarrow 4I_{13/2}, 4F_{9/2} \rightarrow 4I_{13/2}\) in NaYF\(_4\): Yb\(^{3+}\), Er\(^{3+}\)–Codoped NaYF\(_4\) Nanocrystals as a function of temperature.
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decreases, due to the increase of the surface-to-volume ratio compared with the bulk, a large number of NO$_2^-$ and OH$^-$ are involved, with vibrational energies of 1350 and 3350 cm$^{-1}$, respectively, and have available large vibrational quanta to efficiently depopulate the excited states $^4$I$_{11/2}$ and $^4$S$_{3/2}$ nonradiatively.$^{13,14}$ Thus, the non-radiative relaxation becomes more efficient than thermal excitation. The other factor is the thermally activated distribution of electrons among $^4$S$_{3/2}$. Some of electrons can be thermally excited into $^2$H$_{11/2}$ from $^4$S$_{3/2}$ as the temperature increases. That also decreases the green emissions from $^4$S$_{3/2}$.

4. SUMMARY

In conclusion, Yb$^{3+}$, Er$^{3+}$-codoped fluoride nanocrystals were synthesized. These crystals demonstrate high crystal quality and excellent dispersivity and can be transparently dispersed in nonpolar solvents. At the same time, the transparent colloidal solution shows efficient infrared-to-visible UC emission. The green upconversion luminescence exhibited a four-fold intensity enhancement when the temperature of the sample was varied in the range between 20 K and 300 K with the maximum intensity attained around 160 K. The excellent luminescence of hexagonal-phase NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ nanocrystals provides the basis for a more thorough investigation of their optical and temperature properties and might enable applications in nanoscale biological imaging or displays.

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References and Notes


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