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Femtosecond laser induced cross relaxation in Er$^{3+}$ doped NaYF$_4$ glass ceramic

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Abstract
Cross relaxation (CR) plays a significant role in the luminescence of rare-earth ion doped materials. It is generally considered as a major cause of concentration quenching in bulky materials and has been intentionally adopted in selectively tuning the color output. In this work, we combine streak camera with spectrometer to investigate the CR processes in Er$^{3+}$ doped NaYF$_4$ glass ceramic under a 400 nm femtosecond laser field. This combination technique incorporates the advantages of both the streak camera with high time-resolution and the spectrometer with good wavelength-resolution, and can provide the luminescence information in both the temporal and spectral dimensions. A new CR process is experimentally observed in the higher doping concentration, and its excitation mechanism is justified by comparing the luminescence lifetimes and intensities in low and high doping concentrations. This study will contribute to a better understanding of the luminescence mechanisms in the rare earth ion doped materials and its color output tuning.

Keywords: cross relaxation, energy transfer, rare earth ions, femtosecond laser

(Some figures may appear in colour only in the online journal)

1. Introduction

Energy transfer (ET) is one of major luminescence mechanisms in the lanthanide ion doped materials [1–6]. As a particular ET process, cross relaxation (CR) refers to the type of downconversion ET occurring between identical rare earth ions [7]. Generally, the CR process is considered to be deleterious to the luminescence efficiency of rare earth ions [8–10], and it is also regarded as the major cause of the concentration quenching of luminescence in bulky materials [11, 12]. However, the CR process has its inherent advantages, which can be used to selectively tune the color output in the luminescence. For example, Zhang et al reported the CR process induced upconversion enhancement in Tm$^{3+}$ ion doped NaYF$_4$: Yb/Tm nanoparticles [13]; Wei et al experimentally obtained the pure red upconversion in activator- and sensitizer-rich lanthanide nanoparticles via the CR process [14];
Zhao et al demonstrated the upconversion color modulation in Er$^{3+}$ ion doped Gd$_2$O$_3$ host induced by the CR and non-steady-state processes [15]. Therefore, the CR process has become a recent research hotspot in the luminescence of rare earth ion doped materials.

In previous works, the CR process has been widely studied by various measurement methods [16–18]. The time-resolved dynamic measurement is the most direct way to observe the CR process [19]. In this work, we experimentally study the 400 nm femtosecond laser induced CR process in Er$^{3+}$ doped NaYF$_4$ glass ceramic by combining streak camera with spectrometer. The combination of streak camera and spectrometer has the important advantage that can obtain both the time- and wavelength-resolved luminescence information, which is especially suitable for studying the luminescence dynamics in the rare earth ions. As the direct evidence of the ET process, a time-delayed luminescence process is experimentally observed in the higher doping concentration. By considering the luminescence lifetimes and intensities in the low and high doping concentrations, a new CR process in Er$^{3+}$ ions is proposed to explain the experimental observation.

2. Experimental arrangement

The experimental setup is shown in figure 1. Here, a Ti:sapphire mode-locked regenerative amplifier is used as the excitation source with a pulse duration of 50 fs, central wavelength of 800 nm and repetition rate of 1 kHz. The output laser is guided into a nonlinear β-BBO crystal for generating frequency doubling. The mixed lasers are reflected by a dichroic mirror (400 nm reflection and 800 nm transmission), and then pass through a low-pass-filter (cutting wavelength 600 nm) in order to eliminate the residual 800 nm laser. Finally, the 400 nm laser is focused into the measured sample by using a lens with 200 mm focus length. The luminescence signals emitted from the glass ceramic sample are picked up by two collecting lens in the vertical direction of laser propagation, and then are steered into a grating spectrometer (Princeton Instrument 2300i) and a streak camera (HAMAMMATSU C7700) for spectral and dynamical measurements.

In our experiment, 1% Er$^{3+}$ and 5% Er$^{3+}$ doped NaYF$_4$ glass ceramics are designed with the following compositions: 40SiO$_2$–25Al$_2$O$_3$–18Na$_2$CO$_3$–10YF$_3$–7NaF–1ErF$_3$ (mol.%) and 40SiO$_2$–25Al$_2$O$_3$–18Na$_2$CO$_3$–10YF$_3$–7NaF–5ErF$_3$ (mol.%). The high purity raw materials are first mixed and melted in a covered platinum crucible at the temperature of 1450 °C for 45 min in air atmosphere, and then are cast into a brass mold followed by annealing at the temperature of 450 °C for 10 h. The synthesized glass ceramic is heated to the temperature of 600 °C with an increase rate of 10 °C per minute. The glass ceramic is kept at this temperature for 2 h, and then cooled down to room temperature to form a glass ceramic via crystallization. Finally, the two glass ceramic samples are further cut and polished prior to the optical measurements.

3. Results and discussion

The x-ray diffraction (XRD) analysis is a universal method to identify the crystallization phase, and the transmission electron microscopy (TEM) is conventionally used to characterize the nanocrystal size. The XRD curves and TEM images of both 1% Er$^{3+}$ and 5% Er$^{3+}$ doped NaYF$_4$ glass ceramics have been presented in our previous works [20,21], and are omitted here to avoid redundancy. The XRD sharp peaks showed a diffraction pattern of a crystalline structure that can be ascribed to cubic α-NaYF$_4$ crystal for both glass ceramics samples. The TEM results showed that the nanocrystals disperse uniformly in the glass matrix with an average size of 20–30 nm. The high-resolution TEM (HRTEM) images with individual α-NaYF$_4$ nanocrystals further indicated that the lattice fringe spacing of both 1% Er$^{3+}$ and 5% Er$^{3+}$ doped NaYF$_4$ crystals were very close with their values being 0.30 and 0.31 nm, respectively.

The UV–VIS–NIR absorption spectrum of 1% Er$^{3+}$ doped glass ceramic is measured by a U-4100 spectrophotometer, and the result is shown in figure 2(a). Six absorption bands centered at 404, 485, 518, 542, 650 and 798 nm can be clearly observed, which can be attributed to the transitions from the ground state 4I$_{15/2}$ to these excited states 2H$_{9/2}$, 4F$_{7/2}$, 2H$_{11/2}$, 4I$_{15/2}$/2H$_{11/2}$, 4S$_{3/2}$, 4F$_{9/2}$ and 4I$_{11/2}$, respectively. The luminescence spectra of both 1% Er$^{3+}$ and 5% Er$^{3+}$ doped glass ceramic samples with 400 nm femtosecond laser excitation are obtained by using a fiber spectrometer (Ocean Optics MayaPro), and the experimental results are given in figure 2(b). As can be seen, there are four major emission bands around 544, 654, 848 and 975 nm, these luminescence signals can be assigned to these state transitions 4S$_{3/2}$ → 4I$_{15/2}$, 2H$_{11/2}$ → 4I$_{15/2}$, 4F$_{9/2}$ → 4I$_{15/2}$, 4S$_{3/2}$ → 4I$_{11/2}$, and 4I$_{11/2}$ → 4I$_{15/2}$, respectively. Obviously, the green emission around 544 nm and the red emission around 654 nm dominate the visible component of the luminescence spectra. When the Er$^{3+}$ doping concentration is up to 5% from 1%, the intensity ratio of the red emission at 654 nm to the green one at 544 nm increases. This red/green color output tuning by controlling the Er$^{3+}$ doping concentration has been demonstrated in previous studies under various excitation sources [22–26].
Figure 2. UV–VIS–NIR absorption spectrum of 1% Er$^{3+}$ doped glass ceramic (a); luminescence spectra of 1% Er$^{3+}$ (cyan line) and 5% Er$^{3+}$ (red line) doped glass samples with 400 nm femtosecond laser excitation (b).

Figure 3. Streak camera recorded luminescence dynamic processes of green (a), (c) and red (b) and (d) luminescence in 1% Er$^{3+}$ (a) and (b) and 5% Er$^{3+}$ (c) and (d) doped glass samples with 400 nm femtosecond laser excitation (left), together with time-dependent wavelength-integrated luminescence intensities (right).
Taking advantage of the streak camera combined with spectrometer, we can obtain the wavelength-resolved luminescence dynamic process. Figure 3 shows the temporal evolution behaviors of green and red luminescence in 1% Er³⁺ and 5% Er³⁺ doped glass ceramic samples with 400 nm femtosecond laser excitation. The vertical ordinate corresponds to the time delay with respect to the femtosecond laser pulse, and the horizontal ordinate indicates the luminescence wavelength. To more clearly observe the luminescence process, the wavelength-integrated luminescence intensity evolution is also given in figure 3. For 1% Er³⁺ doped glass ceramic sample, both the green and red luminescence intensities decrease with an exponential function, which is the conventional characteristics of luminescence decay. For 5% Er³⁺ doped glass ceramic sample, the decay behavior of green luminescence remains an exponential way, but that of the red emission shows a different way with an obvious rising edge. The slow rising edge in the luminescence process is conventionally considered as a sign of the ET process [27, 28].

To explore the ET process in our experiment, the energy level diagram of Er³⁺ ions is presented in figure 4, together with the possible emission transitions and ET processes with 400 nm femtosecond laser excitation. In previous studies, three ET processes are conventionally recognized [14, 29, 30], i.e. ETU① 4I11/2 → 4I13/2 → 4F9/2 + 4I15/2; ETU② 24I11/2 → 2H11/2 + 4I15/2 and CR① 4F7/2 + 4I11/2 → 24F9/2. Here, ETU②, ETU① and CR① are all phonon-assisted ET processes. The energy mismatches for ETU①, ETU② and CR① are about 1350, 1250 and 200 cm⁻¹ [31], and the mean phonon energy for the NaYF₄ glass ceramic substrate is about 360 cm⁻¹ [32]. Consequently, the three phonon-assisted ET processes (i.e. ETU①, ETU② and CR①) require relatively large population in the involved states. As shown in figure 4, the state 4I11/2 is involved in all the three ET processes, and thus its population determines the efficiencies of ETU①, ETU② and CR①. The luminescence intensity at 975 nm, corresponding to the state transition 4I11/2 → 4I15/2, can be served as an indication of the state 4I11/2 population. As shown in figure 2(b), the luminescence intensities at 975 nm in the low and high doping concentrations are relatively low, which mean the small population in the state 4I11/2. The state 4F7/2 is involved in the CR① process, and its population can be reflected by measuring the luminescence intensity at 485 nm, corresponding to the state transition 4F7/2 → 4I15/2. However, no discernible luminescence signal appears around 485 nm, as shown in figure 2(b). Moreover, the ETU① and ETU② processes contribute to the red and green luminescence, respectively. If the ETU① and ETU② processes do occur efficiently in our experiment, the similar rising edge in the green luminescence process should be observed. However, no such experimental phenomenon is found, as shown in figure 3(c). Based on these experimental observations, we believe that the contributions of ETU①, ETU② and CR① to the ET process in our experiment should be relatively small, which is different from the previous studies.

Based on the above discussion and analysis, we speculate that a new ET process should be involved in our experiment.
Considering the energy levels of Er\(^{3+}\) ions and the possible transition pathways, we propose the following new CR\(^{2}\) process:

\[
\text{\(^2\)H}_{\text{9/2}} + \text{\(^4\)I}_{\text{13/2}} \rightarrow \text{\(^2\)F}_{\text{9/2}}
\]

as shown in figure 4. The energy mismatch for the CR\(^{2}\) process is about 550 cm\(^{-1}\) [30], which is a moderate value for the phonon-assisted ET process. With 400 nm femtosecond laser excitation, the state \(^2\)H\(_{9/2}\) is heavily populated by single-photon absorption, and emits the green fluorescence of 554 nm by decaying to the state \(^4\)I\(_{13/2}\), i.e. \(^2\)H\(_{9/2}\) \(\rightarrow\) \(^4\)I\(_{13/2}\). Furthermore, a large number of population will rapidly decay to those lower states either radiatively or non-radiatively, like \(^2\)H\(_{11/2}\), \(^4\)S\(_{3/2}\) and \(^4\)F\(_{9/2}\), and emits the green fluorescence of 524 nm (\(^2\)H\(_{11/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\)) and \(^544\) nm (\(^4\)S\(_{3/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\)) and the red fluorescence of 654 nm (\(^4\)F\(_{9/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\)). Figure 5 shows the NIR luminescence spectra of 1\% Er\(^{3+}\) (blue line) and 5\% Er\(^{3+}\) (red line) doped glass samples with 400 nm femtosecond laser excitation.

The CR\(^{2}\) process can help to transfer the population from the state \(^2\)H\(_{9/2}\) to the state \(^2\)F\(_{9/2}\), and thus will suppress the green luminescence and enhance the red one. As shown in figure 2(b), the increase of the red/green luminescence intensity ratio can well explain the population transfer when the Er\(^{3+}\) doping concentration is increased to 5\% from 1\%.

To ensure that the CR\(^{2}\) process occurs, the state \(^4\)I\(_{13/2}\) population is also critical. The state \(^4\)I\(_{13/2}\) can emit the near-infrared fluorescence at 1533 nm via the state transition \(^4\)I\(_{13/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\). Similarly, in order to examine the state \(^4\)I\(_{13/2}\) population, we measure the near-infrared luminescence spectra in 1\% Er\(^{3+}\) and 5\% Er\(^{3+}\) doped glass ceramic samples, and the measured results are shown in figure 5. It can be seen that the luminescence intensity at 1533 nm is much higher than that at 975 nm, which means more population in the state \(^4\)I\(_{13/2}\) compared to the state \(^4\)I\(_{11/2}\). As discussed above, the state \(^4\)I\(_{11/2}\) is involved in the ETU\(^{1}\), ETU\(^{2}\) and CR\(^{1}\) processes. This phenomenon further justifies our speculation that the CR\(^{2}\) process should play a much more important role than the ETU\(^{1}\), ETU\(^{2}\) and CR\(^{1}\) processes in our experiment.

As shown in figure 4, the CR\(^{2}\) process can help to deplete the state \(^2\)H\(_{9/2}\) population by transferring it to the state \(^2\)F\(_{9/2}\). Thus, the 554 nm (\(^2\)H\(_{9/2}\) \(\rightarrow\) \(^4\)I\(_{13/2}\)) luminescence lifetime will be shortened due to the CR\(^{2}\) process. However, the state \(^4\)S\(_{3/2}\) population comes from the rapid relaxation of the state \(^2\)H\(_{9/2}\), which should be almost unaffected by the relatively slow CR\(^{2}\) process, and thus the 544 nm (\(^4\)S\(_{3/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\)) luminescence lifetime should keep unchanged. To verify this speculation, we compare the 544 and 554 nm luminescence lifetimes in 1\% Er\(^{3+}\) and 5\% Er\(^{3+}\) doped glass ceramic samples, as shown in figure 6. These data are extracted from figures 3(a) and (c). Here, a monoexponential function is used to fit the luminescence intensity decay, and the fitting time constant is considered as the luminescence lifetime. With the increase in the Er\(^{3+}\) doping concentration from 1\% to 5\%, the 554 nm luminescence lifetime decreases from 5.18 to 4.14 \(\mu\)s, which is reduced up to about 20\%, while the 544 nm luminescence lifetime decreases to 6.15 from 6.47 \(\mu\)s, which is only reduced by about 5\%. Here, this slight decrease in the luminescence lifetime may be due to a change in the Er\(^{3+}\) doping concentration. Obviously, such an experimental observation is in good agreement with our prediction, which further confirms the proposed CR\(^{2}\) process in our experiment.

**Conclusions**

In summary, we have experimentally studied the luminescence dynamics in Er\(^{3+}\) doped NaYF\(_4\) glass ceramics with the 400 nm femtosecond laser excitation by combining streak camera and spectrometer. This combined measurement...
technique can provide both the temporal and spectral information in the luminescence of rare earth ions. Based on the measured time- and wavelength-resolved luminescence spectra, we observed a time-delayed luminescence process, which was the direct evidence of the ET process. By comparing the luminescence lifetimes and intensities in the low and high Er$^{3+}$ doping concentrations, we successfully assigned a new CR process. This work provides a clear physical insight to explain the CR process in the rare earth ions, which is very helpful for understanding the luminescence mechanism in the rare earth ion doped materials, and should have important scientific significance in relevant application fields.

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