Upconversion of Er³⁺ Ions in LiKGdF₅:Er³⁺, Dy³⁺ Single Crystal Produced by Infrared and Green Laser

Cao Hui (曹 晖)[1,2*], Yin Min (尹 民)[3], Zhang Weiping (张卫平)[3]

(1. Department of Physics, Zhejiang Normal University, Jinhua 321004, China; 2. Zhejiang Key Laboratory for Reactor Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China; 3. Department of Physics, University of Science and Technology of China, Hefei 230026, China)

Abstract: The upconversion fluorescence of Er³⁺ ions in LiKGdF₅:Er³⁺, Dy³⁺ single crystal was studied under 785, 514.5, and 980 nm laser excitation. With the laser excitation of at 785 nm, strong green (centered at 543 nm) upconversion emission, as well as weak red (651 nm), violet (406 nm), and blue (470 nm) upconversion emissions were obtained. With 514.5 nm laser excitation, violet (406 nm) and blue (470 nm) upconversion emissions were observed. Under 980 nm laser excitation, strong green (543 nm) and weak red (651) emissions were also obtained. The laser power dependence of the upconversion emissions are investigated to understand the upconversion mechanism. The excited state absorption (ESA) and the energy transfer (ET) processes were discussed as the possible mechanisms for all upconversion emissions.

Key words: upconversion; LiKGdF₅:Er³⁺; excited state absorption; energy transfer; rare earths

In the past decades, the upconversion of infrared light to visible light of different materials, such as single crystals, optical fibers, and glasses, has been investigated extensively for a wide range of applications, including all-solid compact laser devices operating in the violet-blue-green region, infrared quantum counter detectors, temperature sensors, and fluorescent labels for sensitive detection of biomolecules and optical data storage[1–10]. More recently, exploration on infrared to visible to violet and ultraviolet (UV) upconversion fluorescence has become considerably more significant because it may be useful for new tunable all-solid-state lasers operating in the violet and UV region[14]. In the upconversion process, two (or more) low-energy photons from the excitation source are converted into one photon with higher energy.

Since the intermediate levels ⁴I₁₁/₂ (around 15491 cm⁻¹) and ⁴I₉/₂ (around 10375 cm⁻¹) of Er³⁺ ions can be conveniently populated by commercial low-cost high-power near-infrared laser diodes, Er³⁺ ion doped materials are well suited for upconversion[3,7–13]. Most upconversion studies of Er-doped materials were focused on infrared laser excitation.

However, investigation on violet and blue upconversion under visible laser excitation is very scarce[4,7,11,12]. This upconversion phenomenon is yet to be explored. Fortunately, the ⁴S₃/₂ level, which has a longer lifetime than that of the other states in the visible range, provides an available intermediate state for such exploration[7,10].

It is well established that the luminescence efficiency of rare earth ions is governed principally by the nonradiative process of materials, and the highest phonon frequencies of the host materials are responsible for the nonradiative relaxation rate[13, 14]. Therefore, by selecting a host matrix that has lower phonon energy, high upconversion efficiency can be obtained. Fluoride crystals have been demonstrated as one of the best host materials, benefiting from their low phonon energy, wide transparent region, and their good physical and chemical stability[6, 16, 18].

In this article, the upconversion fluorescence of Er³⁺ ions in LiKGdF₅:Er³⁺, Dy³⁺ single crystal was studied under 785, 514.5 and 980 nm laser excitation. The laser power dependence of the upconverted emissions was investigated to understand the upconversion mechanism. The excited state absorption (ESA) and the energy transfer (ET) processes were discussed as the possible mechanism for all upconversion emissions.

1 Experimental

LiKGdF₅ single crystal co-doped with Er³⁺ (2%) and Dy³⁺ (0.4%) was prepared using the hydrothermal method. The synthesis process was similar to that given in Ref.[14].

The upconversion spectra, excited by 785 and 514.5 nm laser, were measured and analyzed using a Jobin-Yvon LABRAM-HR laser microraman spectrometer system. For temperature dependent studies, samples were placed in a circulating liquid nitrogen cryostat and the temperature was set between 90 and 300 K.

Green and red upconversion emissions, excited by a 980 nm diode laser, were dispersed by a Jobin-Yvon HRD1 double monochromator and were detected using a Hamamatsu R456 photomultiplier. The signal was analyzed by the EG&G 7265 DSP lock-in amplifier and was stored in the computer memory.

2 Results and Discussion

2.1 Pumping with 785 nm laser

Fig.1(a) shows the room temperature upconversion spectra of LiKGdF₅:Er³⁺, Dy³⁺ single crystal under 785 nm laser excitation. The upconversion spectra show bands centered at 522 nm, 543 nm (green), and 651 nm (red), which are attributed to the $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er³⁺ ions, respectively. In addition to these bands, very weak emissions at 406 nm (violet) and 470 nm (blue) are also observed and attributed to the $^2P_{3/2} \rightarrow ^4I_{15/2}$ and $^2P_{3/2} \rightarrow ^4I_{13/2}$ transitions of Er³⁺ ions, respectively[15].

To understand the mechanism of the observed upconversion luminescence, the upconverted luminescence intensity I of these transitions was measured as a function of the pump power P. In the upconversion process, I is proportional to the nth power of P, i.e.,

$$I \propto P^n \qquad (1)$$

where, n is the number of pump photons required to populate the emitting state. A plot of $\lg I$ versus $\lg P$ yields a straight line with slope n. The power dependence of I is shown in Fig.2(a, b). The slopes obtained were 1.93, 1.97, and 1.69 for 522, 543, and
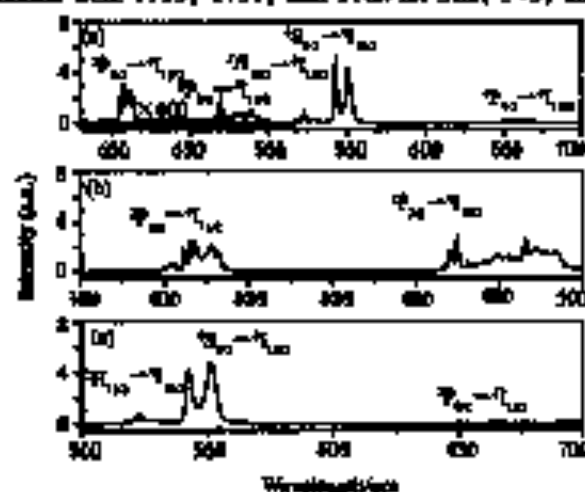

Fig.1 Room temperature upconversion spectra of LiKGdF₅: Er³⁺, Dy³⁺ single crystal
(a) λ_{ex} = 785 nm; (b) λ_{ex} = 514.5 nm; (c) λ_{ex} = 980 nm
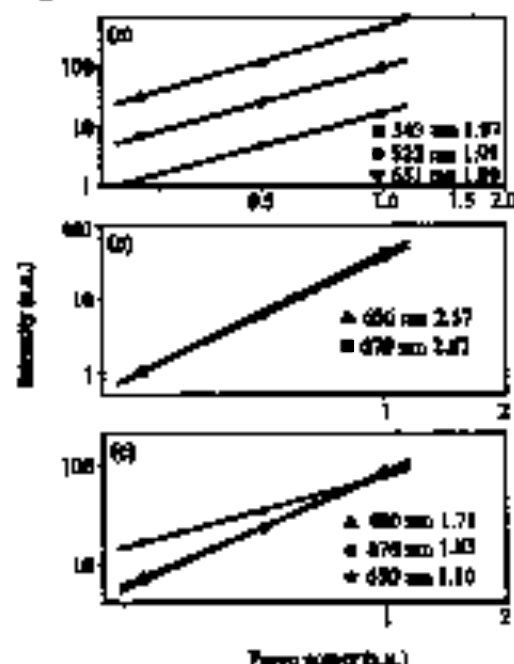
Fig.2 Dependence of the upconversion emission intensity on excitation power for LiKGdF₅:Er³⁺, Dy³⁺ single crystal
(a) λ_{ex} = 785 nm (for green and red emissions); (b) λ_{ex} = 785 nm (for violet and blue emissions); (c) λ_{ex} = 514.5 nm

651 nm emissions, respectively. The results show that two-photon processes contribute to the green and red emissions. For 405 and 470 nm emissions, the n values obtained were 2.57 and 2.57, respectively. This result strongly indicates that three-photon processes contribute to the violet and blue emissions.

The mechanisms of visible emissions of Er^{3+} ions under excitation into the $^4I_{9/2}$ level have been well discussed in the literatures, which involve two well-known upconversion mechanisms: (1) the excited state absorption (ESA), and (2) the energy transfer (ET). The upconversion paths in $LiKGdF_5 : Er^{3+}$, Dy^{3+} are now analyzed. Fig.3(a) provides the energy level diagram of Er^{3+} ions and the probable upconversion mechanisms under 785 nm laser excitation.

When the $^4I_{9/2}$ level of Er^{3+} is directly excited with 785 nm laser, the initial $^4I_{9/2}$ level population relaxes to long lifetime $^4I_{11/2}$ and $^4I_{13/2}$ levels. The ions in $^4I_{11/2}$ level sequentially absorb another 785 nm photon and are raised to $^4F_{3/2,5/2}$ levels (labeled as ESA1). The ions in $^4I_{13/2}$ level can also absorb another 785 nm photon and are raised to the $^2H_{11/2}$ level (ESA2). The ions in $^4F_{3/2,5/2}$ and $^2H_{11/2}$ levels undergo multi-phonon relaxation to $^4H_{11/2}$ and $^4S_{3/2}$ levels and provide green emissions. There is a possible ET route that can also populate these luminescent levels. An excited ion relaxes from the $^4I_{9/2}$ level to the $^4I_{13/2}$ level nonradiatively and transfers the excitation energy to the neighboring ion in the same level, thus promoting the latter to the $^4F_{7/2}$ level: $^4I_{9/2} + ^4I_{9/2} \rightarrow ^4I_{13/2} + ^4F_{7/2}$ (ET1). It must be mentioned that the ET1 process is a phonon-assisted process (absorbing phonon) with an energy mismatch of about 200 cm^{-1}. The $^4F_{9/2}$ level can be possibly pumped via a nonradiative relaxation through the $^4S_{3/2}$ excited state at moderate rate.

As stated above, the power dependence of the 405 ($^2P_{3/2} \rightarrow ^4I_{11/2}$ transition) and 470 nm ($^2P_{3/2} \rightarrow ^4I_{11/2}$ transition) emissions indicates that a three-photon process is involved. The $^2P_{3/2}$ state is populated by the following mechanism: When the $^4S_{3/2}$ level is populated, the ions in the $^4S_{3/2}$ level can absorb another 785 nm photon and are raised to the $^2P_{3/2}$ level (ESA3).

To obtain a firm idea on the nature of the upconversion mechanisms, the effect of temperature on the upconversion luminescence has been investigated as shown in Fig.4. Two phenomena were observed in this figure.

One is that almost no spectral line around 522 nm ($^2H_{11/2} \rightarrow ^4I_{15/2}$ emission) could be observed in Fig.4 (3). This is because the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels is about 720 cm^{-1} and the population of Er^{3+} ions in these two levels depends on the thermal equilibrium distribution. At room temperature, these two levels have almost the same population, whereas at 90 K, the population of the $^2H_{11/2}$ level is very low.

The other phenomenon is that the intensities of green lines corresponding to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition and the intensities of red lines decrease with the decreasing temperature. Such a phenomenon is caused by the fact that the ET1 process is a phonon-assisted process (absorbing phonon) and the energy mismatch is about 200 cm^{-1}. At low temperature (90 K), the rate of the ET1 process decreases considerably and hence the emission intensity decreases.

2.2 Pumping with 514.5 nm laser

Fig.1(b) shows the room temperature upconversion spectra of $LiKGdF_5 : Er^{3+}$, Dy^{3+} single crystal under 514.5 nm laser excitation. The upconversion spectra show bands centered at 405 and 470 nm, which are attributed to the $^2P_{3/2} \rightarrow ^4I_{11/2}$ and $^2P_{3/2} \rightarrow ^4I_{11/2}$

Fig.3   Energy level diagram of Er^{3+} ions in $LiKGdF_5 : Er^{3+}$, Dy^{3+} single crystal and upconversion mechanism
(a) λ_{ex} = 785 nm; (b) λ_{ex} = 514.5 nm; (c) λ_{ex} = 966 nm
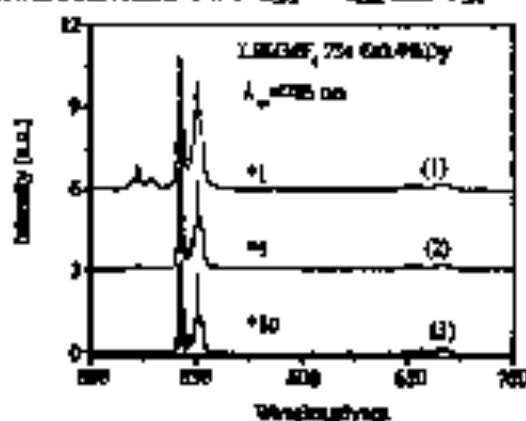

Fig.4   Upconversion luminescence spectra of $LiKGdF_5 : Er^{3+}$, Dy^{3+} single crystal at different temperatures
(1) 300 K, (2) 150 K and (3) 90 K

transitions of Er^{3+} ions, respectively[7]. The bands in the region of 477 ~ 500 nm may arise from the $^4F_{7/2} \rightarrow ^4I_{11/2}$ transition of the Er^{3+} ion.

Fig. 2(c) shows the intensity dependence of the upconversion emissions versus the pump power. The slope n for 405, 477, and 486 nm was 1.71, 1.83, and 1.10, respectively. This result indicates that two-photon processes contribute to the emissions from the $^2P_{3/2}$ level and that the one-photon process pumps the ions at the $^4F_{7/2}$ level. The energy mismatch between the emission at 486 nm and the excitation laser wavelength 514.5 nm amounts to 1140 cm⁻¹. Taking into account the thermal population (at room temperature) of Stark components of the $^4I_{15/2}$ level, Er^{3+} ions can be excited from the ground state to the $^4F_{7/2}$ level by absorbing one 514.5 nm photon with the assistance of phonon.

Fig. 3(b) depicts the probable upconversion mechanisms[11]. Under 514.5 nm laser excitation, Er^{3+} ions are first excited from ground state to $^2H_{11/2}$ or $^4F_{7/2}$ levels by absorbing one pump photon, and then relax quickly to the lower long lifetime level $^4S_{3/2}$. The ions in the $^4S_{3/2}$ level sequentially absorb another 514.5 nm photon and are raised to the $^2P_{3/2}$ level (ESA4). There is a possible ET route that can also populate these luminescence levels. An excited ion relaxes from the $^4S_{3/2}$ level to the $^4I_{13/2}$ level nonradiatively and transfers the excitation energy to the neighboring ion in the same level, promoting it to the $^4G_{11/2}$ level: $^4S_{3/2} + ^4S_{3/2} \rightarrow ^4I_{13/2} + ^4G_{11/2}$ (ET2). Finally, the ions relax to the $^2P_{3/2}$ level through multi-phonon nonradiative processes, and then provide the upconversion luminescence.

The low temperature upconversion spectra of LiKGdF₅:Er³⁺, Dy³⁺ single crystal excited by 514.5 nm laser (not shown here) indicate that the intensities of emissions from the $^2P_{3/2}$ level (405 and 470 nm) increase with the decreasing temperature and almost no emission from the $^4F_{7/2}$ level was observed at 90 K. The former is caused by the fact that at low temperature, there is more population to the $^2P_{3/2}$ level because of the low nonradiative rate. The latter one confirmed that the $^4F_{7/2}$ level is populated via absorbing one 514.5 nm photon from the Stark components of the ground state.

2.3 Pumping with 980 nm laser

Fig. 1(c) shows the room temperature upconversion spectra of LiKGdF₅:Er³⁺, Dy³⁺ single crystal excited by 980 nm laser. The bands centered at 522, 551, and 651 nm are assigned to the $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} ions, re-

spectively, which is identical to Fig. 1(a).

The intensity dependence of the upconversion emissions versus the pump power (figure not shown here) shows the slope n for 522, 551, and 651 nm ~ 2, which indicates the two-photon processes contribute to the green and red emissions.

The probable upconversion mechanisms are presented in Fig. 3(c)[10,11]. Under 980 nm excitation, Er^{3+} ions are excited from the ground state to the $^4I_{11/2}$ level by absorbing one 980 nm laser photon (ESA5). Ions in the $^4I_{11/2}$ level sequentially absorb another 980 nm photon and are raised to the $^4F_{7/2}$ level. Ions in the $^4F_{7/2}$ level undergo multi-phonon relaxation to luminescent levels $^2H_{11/2}$ and $^4S_{3/2}$ and provide green emissions from these two levels. In addition, the contribution of the ET1 process cannot be rejected. The luminescent level $^4F_{9/2}$ can be populated via nonradiative relaxation from the $^4S_{3/2}$ excited state.

3 Conclusion

Violet, blue, green, and red upconversion luminescence emissions of Er^{3+} in LiKGdF₅:Er³⁺, Dy³⁺ single crystal were observed under 785, 514.5, and 980 nm laser excitation. The excited state absorption and the energy transfer process were discussed as possible mechanisms for all the upconversion emissions. In conclusion, the LiKGdF₅:Er³⁺, Dy³⁺ single crystal is a very promising crystal material to obtain violet or visible upconversion emission.

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