Two-photon, three-photon, and four-photon near-infrared quantum cutting luminescence of an Er\(^{3+}\) activator in tellurium glass phosphor

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Multiphoton near-IR downconversion quantum cutting luminescence of Er\(^{3+}\)-ion-doped tellurium glass is studied. We find that the excitation spectra of 1532.0 nm IR light and 550.0 nm visible light are very similar in waveform and peak wavelength. When the concentration of Er\(^{3+}\) ions is increased from 0.5% to 3.2%, we observe that both the IR luminescence and excitation intensity of the samples are increased by a factor of 1.80–5.49, with a concomitant decrease in both visible luminescence and excitation intensity by a factor of 0.87–1.91. Therefore, we conclude that the present phenomenon is a multiphoton near-IR quantum cutting luminescence phenomenon. We also find that the near-IR quantum cutting efficiency up-limits of the \(^{4}\text{I}_{9/2}, \ ^{4}\text{F}_{9/2}, \ ^{4}\text{S}_{3/2}, \) and \(^{2}\text{H}_{11/2}\) states are respectively 157%, 138%, 193%, and 192% for Er\(^{3+}\)(3.2%):tellurium glass and 175%, 154%, 233%, and 233% for Er\(^{3+}\)(5.0%):tellurium glass. © 2016 Optical Society of America

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1. INTRODUCTION

The gradual exhaustion of traditional fossil energy sources and the pollution of the environment have increasingly restricted the sustainable development of people and society [1,2]. Thus, the energy source crisis has become the main bottleneck in the development of society, and finding and utilizing new energy sources has become an important project globally [1–10]. Converting solar energy directly into electrical energy is an effective method for resolving the energy source crisis [1–20]. It is a focus of research for many scientists. Solar energy has been praised as the ideal new energy source. However, there is a great disparity between its huge reserves and low actual utilization, mainly because energy conversion must be achieved across the entire solar spectrum, from UV and visible light to near-IR [5–12]. The greatest efficiency achieved for a commercial crystalline Si solar cell is currently around 15%. The theoretical efficiency of a normal single-junction crystalline silicon (c-Si) solar cell is limited to 30% of the Shockley–Queisser limit [9,14]. Much energy is lost through (1) lattice thermalization loss, (2) transparency loss, (3) recombination loss, (4) junction loss, and (5) contact voltage loss. Of these, losses of more than 70% are due to spectral mismatch losses in transmission loss and thermalization loss [12–22]. These are mainly due to the spectral mismatch losses between the radiated photon energy of the Sun and the energy bandgap \(E_g\) of solar cells. That is, for the higher-energy photons whose energy is larger than \(E_g\), most of the photon energy is wasted in the conversion. The surplus energy (\(h\nu-E_g\)) is converted to the kinetic energy of the electron–hole pair, which is subsequently converted to the heat energy of the matrix (thermalization loss). However, lower-energy photons whose energy is smaller than \(E_g\) cannot be absorbed by semiconductor materials (transmission loss). Therefore, the sensitivity of the spectral responsivity of a solar cell can be enhanced greatly if we put an Er\(^{3+}\) activated phosphor on the front of a germanium (Ge) or amorphous silicon (a-Si) solar cell to construct the multiphoton quantum cutting solar cell. First, the energy bandgap \(E_g\) of Ge or a-Si, which is about 0.67 eV (1850–2000 nm) [23], is...
much smaller than that of c-Si, which is about 1.12 eV (1100 nm), and thus the IR solar spectral energy can be utilized more abundantly. Second, the higher-energy photon with a wavelength between 250 and 400 nm, between 400 and 550 nm, or between 550 and 800 nm can be divided into four, three, or two lower-energy photons, respectively, with wavelengths about 1550 nm, using a quantum cutting method of Er$^{3+}$ activator [1,9,23]. Thus the photoluminescence efficiency can obviously exceed 100%, and the electricity generating efficiency can obviously exceed 30% of the Shockley–Queisser limit. Moreover, recombination loss can also be reduced by using a quantum cutting method. Therefore, a near-IR quantum cutting luminescence solar cell has excellent potential for application in solar cell devices [5–22].

Trupke et al. originally proposed the theory of “improving solar cell efficiencies by downconversion of high-energy photons” in 2002 [10]. They reported that the maximum theoretical efficiency can reach 38% for a two-photon quantum cutting silicon solar cell with the practical geometry of a luminescence converter on the front surface. It exhibited sensitivity to solar light in the range of 280–1100 nm [10]. Vergeer et al. were the first to report on experimental “quantum cutting by cooperative energy transfer in Yb$_3$Y$_{1-x}$PO$_4$: Tb$^{3+}$” phosphors in 2005 [1], after Wegh et al. had reported on the well-known visible quantum cutting experimental phenomenon in a Eu$^{3+}$–Gd$^{3+}$ system in Science magazine [2]. Since 2007, many research groups including Meijerink and colleagues [1,3], Qiu and colleagues [11], Wang and colleagues [5,6], Zhang and colleagues [7,17], and others [20,21] have reported in more than 200 papers on near-IR quantum cutting luminescence phenomena of sensitizer-Yb$^{3+}$ ion co-doped materials [5–22], which were used to develop two-photon quantum cutting silicon solar cells. Near-IR quantum cutting has become a popular topic globally for research in scientific and optical fields. Meijerink and colleagues [15,19], Qiu and colleagues [9,12], and our group [8,22] have reported on experimental research on multiphoton near-IR quantum cutting in materials doped with Er$^{3+}$ or Tm$^{3+}$ activator ions. These continuing improvements [11] have led to the multiphoton quantum cutting Ge solar cells [3,8,12,14,15,19,22], which are sensitive to wavelengths of 280–1850 nm and are environmentally friendly. Their maximum efficiency can greatly exceed 38% [22]. Thus, these works are very significant. Moreover, the present glass phosphor can be applied to other photovoltaic devices, such as a-Si photovoltaic devices [23].

2. EXPERIMENTAL PROCEDURE

The samples used in our present work are (A) Er$^{3+}$ (3.2%):tellurium glass, (B) Er$^{3+}$ (0.5%):tellurium glass, and (C) Er$^{3+}$ (5.0%):tellurium glass. The constitution of the sample (A) Er$^{3+}$ (3.2%):tellurium glass, for example, is 70TeO$_2$–25ZnO–5La$_2$O$_3$–3.2Er$_2$O$_3$. The tellurium glasses were prepared using highly pure TeO$_2$, ZnO, La$_2$O$_3$, and Er$_2$O$_3$ powders as the starting materials. The well-mixed raw materials for a 50 g batch were placed in an alumina crucible. The samples were melted at 900°C for 50 min under oxygen atmosphere. Dry oxygen gas was introduced in order to remove hydroxyl groups. The melts were then collected in a preheated stainless steel mold and annealed for 2 h near the glass transition temperature, $T_g$, about 300°C. The annealed sample was cut and polished to the size of 16 mm × 20 mm × 5.5 mm for optical measurement.

The equipment used in our experiment is a FL3-2iHR fluorescence spectrometer (Horiba-JY Co., America, Japan, and France). The excitation light source is a Xe lamp. The visible detector is an R2658p photomultiplier. The IR detector is a H10330-75 photomultiplier. For all results, the signal intensities at the same wavelength in the same figure can be compared directly already. The absorption of the sample (A) Er$^{3+}$ (3.2%):tellurium glass was measured using a SPECOLRD 200 spectrophotometer (Analytik-Jena, Germany). The lifetime dynamics are recorded using the FL3-2iHR fluorescence spectrometer, with an excitation wavelength of 378 nm, a measurement range of 340 μs, a peak present of 2.80 × 10$^4$, a sweep present of 1.28 × 10$^5$, and a delay of 0%.

3. ABSORPTION

The absorption spectrum is shown in Fig. 1. We found that the absorption peaks of (A) Er$^{3+}$ (3.2%):tellurium glass are positioned at (1517.2, 1531.5), 976.8, 799.5, 653.2, 544.5, 522.0, 489.0, 451.8, 443.6, 406.8, 379.2, and 365.8 nm. We recognize these absorption peaks as the absorption transitions of $^4$I$_{15/2}$ → $^4$I$_{13/2}$, $^4$I$_{15/2}$ → $^4$I$_{11/2}$, $^4$I$_{15/2}$ → $^4$I$_{9/2}$, $^4$I$_{15/2}$ → $^4$I$_{7/2}$, $^4$I$_{15/2}$ → $^4$I$_{5/2}$, $^4$I$_{15/2}$ → $^4$I$_{3/2}$, $^4$I$_{15/2}$ → $^4$I$_{1/2}$, $^4$I$_{15/2}$ → $^4$I$_{1/2}$, and $^4$I$_{15/2}$ → $^4$I$_{1/2}$ of the Er$^{3+}$ ion [16,18], respectively.

4. EXCITATION

Keeping the experimental settings the same, we measured the excitation spectra of samples (A) Er$^{3+}$ (3.2%):tellurium glass and (B) Er$^{3+}$ (0.5%):tellurium glass. First, we selected a visible luminescence wavelength of 550.0 nm as the receiving wavelength to measure the visible excitation spectra in the range of 250–508 nm, as shown in Fig. 2. We observe five excitation peaks positioned at the 365.5, 378.5, 406.5, 450.5, and 488.5 nm. We recognize that they are respectively the absorption peaks of the $^4$I$_{15/2}$ → $^4$G$_{9/2}$, $^4$I$_{15/2}$ → $^4$G$_{11/2}$, $^4$I$_{15/2}$ → $^4$H$_{9/2}$, $^4$I$_{15/2}$ → $^4$F$_{7/2}$, and $^4$I$_{15/2}$ → $^4$F$_{5/2}$

![Fig. 1. Absorption spectrum of (A) Er$^{3+}$ (3.2%):tellurium glass.](image-url)
transitions of the Er$^{3+}$ ion [16,18]. For the excitation spectrum of 550.0 nm luminescence, we found that the excitation spectrum intensities of (A) Er$^{3+}$ (3.2%):tellurium glass are approximately $3.61 \times 10^6$, $8.33 \times 10^6$, $2.09 \times 10^6$, $1.82 \times 10^6$, and $4.29 \times 10^6$ for the 365.5, 378.5, 406.5, 450.5, and 488.5 nm transitions, respectively; those of (B) Er$^{3+}$ (0.5%):tellurium glass are approximately $3.50 \times 10^6$, $1.59 \times 10^7$, $1.83 \times 10^7$, $1.79 \times 10^7$, and $5.11 \times 10^6$ for the 365.5, 378.5, 406.5, 450.5, and 488.5 nm transitions. We calculated that the excitation spectrum intensities of the 550.0 nm luminescence, we found that the excitation spectrum intensities of (A) Er$^{3+}$ (3.2%):tellurium glass are approximately $9.82 \times 10^6$, $1.86 \times 10^7$, $5.27 \times 10^7$, $4.86 \times 10^6$, $1.03 \times 10^7$, $1.76 \times 10^7$, $4.79 \times 10^6$, $8.51 \times 10^6$, and $3.11 \times 10^6$ for the 365.5, 378.0, 406.5, 450.5, 488.0, 520.5, 543.0, 652.5, and 800.0 nm transitions, respectively; those of (B) Er$^{3+}$ (0.5%):tellurium glass are approximately $2.63 \times 10^6$, $1.01 \times 10^7$, $1.34 \times 10^7$, $1.29 \times 10^6$, $3.34 \times 10^6$, $9.78 \times 10^6$, $1.28 \times 10^7$, $3.78 \times 10^6$, and $1.60 \times 10^6$ for the 365.5, 378.0, 406.5, 450.5, 488.0, 520.5, 543.0, 652.5, and 800.0 nm transitions. We calculated that the excitation spectrum intensities of the IR 1532.0 nm luminescence of (A) Er$^{3+}$ (3.2%):tellurium glass are approximately $3.73 \times 10^6$, $1.85 \times 10^5$, $3.92 \times 10^5$, $3.76 \times 10^6$, $3.08 \times 10^6$, $1.53 \times 10^7$, $3.76 \times 10^6$, $3.92 \times 10^6$, $3.08 \times 10^6$, and $1.53 \times 10^7$ for the 365.5, 378.0, 406.5, 450.5, 488.0, 520.5, 543.0, 652.5, and 800.0 nm transitions. We also found that they are 3.73, 1.85, 3.92, 3.76, 3.08, 1.80, 3.76, 2.26, and 1.95 times larger than those of (B) Er$^{3+}$ (0.5%):tellurium glass for the $4I_{15/2} \rightarrow 4G_{9/2}$, $4I_{15/2} \rightarrow 4G_{11/2}$, $4I_{15/2} \rightarrow 2H_{9/2}$, $4I_{15/2} \rightarrow (4F_{3/2}, 4F_{5/2})$, and $4I_{15/2} \rightarrow 2F_{7/2}$, respectively.

### 5. LUMINESCENCE

Keeping the same experimental conditions, we measured the luminescence spectra of sample (A) Er$^{3+}$ (3.2%):tellurium glass and (B) Er$^{3+}$ (0.5%):tellurium glass. First, we selected the excitation peak at 378.5 nm as the excitation wavelength to measure the visible luminescence spectrum in the range of 395–728 nm, as shown in Fig. 3. We can see that the luminescence peaks are positioned at 406.5, 523.5, 545.0, and 658.0 nm. We recognize that these luminescence peaks are respectively $2H_{9/2} \rightarrow 4I_{15/2}$, $3H_{11/2} \rightarrow 4I_{15/2}$, $3S_{3/2} \rightarrow 4I_{15/2}$, and $4F_{9/2} \rightarrow 4I_{15/2}$ of the Er$^{3+}$ ion [16,18]. We found that the luminescence intensities, when excited by 378.5 nm light, are approximately $7.77 \times 10^4$, $5.20 \times 10^4$, $1.55 \times 10^6$, and $2.71 \times 10^4$ for the $2H_{9/2} \rightarrow 4I_{15/2}$, $3H_{11/2} \rightarrow 4I_{15/2}$, $3S_{3/2} \rightarrow 4I_{15/2}$, and $4F_{9/2} \rightarrow 4I_{15/2}$ of the Er$^{3+}$ ion [16,18]. We found that the luminescence intensities, when excited by 378.5 nm light, are approximately $7.77 \times 10^4$, $5.20 \times 10^4$, $1.55 \times 10^6$, and $2.71 \times 10^4$ for the $2H_{9/2} \rightarrow 4I_{15/2}$, $3H_{11/2} \rightarrow 4I_{15/2}$, $3S_{3/2} \rightarrow 4I_{15/2}$, and $4F_{9/2} \rightarrow 4I_{15/2}$ of the Er$^{3+}$ ion [16,18]. We also recognized that the main luminescence peak of the Er$^{3+}$ ion is approximately $3.73 \times 10^6$, $1.85 \times 10^5$, $3.92 \times 10^5$, $3.76 \times 10^6$, $3.08 \times 10^6$, and $1.53 \times 10^7$ for the 365.5, 378.0, 406.5, 450.5, 488.0, 520.5, 543.0, 652.5, and 800.0 nm transitions.
Table 2. Infrared Excitation Intensity of (A) Er(3.2%):Tellurium Glass and (B) Er(0.5%):Tellurium Glass When the Monitored Wavelength Is Positioned at 1532.0 nm

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Transition</th>
<th>3.2% Intensity</th>
<th>0.5% Intensity</th>
<th>Intensity Proportion of 3.2%/0.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>365.5</td>
<td>4I15/2 → 4G9/2</td>
<td>9.82 x 10^6</td>
<td>2.63 x 10^6</td>
<td>3.73</td>
</tr>
<tr>
<td>378.0</td>
<td>4I15/2 → 4G11/2</td>
<td>1.86 x 10^7</td>
<td>1.01 x 10^7</td>
<td>1.85</td>
</tr>
<tr>
<td>406.5</td>
<td>4I15/2 → 2H9/2</td>
<td>5.27 x 10^6</td>
<td>1.34 x 10^6</td>
<td>3.92</td>
</tr>
<tr>
<td>450.5</td>
<td>4F15/2 → 4F5/2</td>
<td>4.86 x 10^6</td>
<td>1.29 x 10^6</td>
<td>3.76</td>
</tr>
<tr>
<td>488.5</td>
<td>4F15/2 → 4F7/2</td>
<td>1.03 x 10^7</td>
<td>3.34 x 10^6</td>
<td>3.08</td>
</tr>
<tr>
<td>520.5</td>
<td>4I15/2 → 2H11/2</td>
<td>1.76 x 10^7</td>
<td>9.78 x 10^6</td>
<td>1.80</td>
</tr>
<tr>
<td>543.0</td>
<td>4I15/2 → 4S9/2</td>
<td>4.79 x 10^6</td>
<td>1.28 x 10^6</td>
<td>3.76</td>
</tr>
<tr>
<td>652.0</td>
<td>4I15/2 → 4F9/2</td>
<td>8.51 x 10^6</td>
<td>3.78 x 10^6</td>
<td>2.26</td>
</tr>
<tr>
<td>800.0</td>
<td>4I15/2 → 4I1/2</td>
<td>3.11 x 10^7</td>
<td>1.60 x 10^6</td>
<td>1.95</td>
</tr>
</tbody>
</table>

*Intensity I = (Infrared signal S2–Background B)/Excitation light intensity R1.

Fig. 3. 1, Visible luminescence spectra; 2, IR luminescence spectra of sample (A) Er³⁺ (3.2%):tellurium glass (blue) and (B) Er³⁺ (0.5%):tellurium glass (red) when excited by 378.5 nm light.

Fig. 4. 1, Visible luminescence spectra; 2, IR luminescence spectra of sample (A) Er³⁺ (3.2%):tellurium glass (blue) and (B) Er³⁺ (0.5%):tellurium glass (red) when excited by 488.0 nm light.

respectively. We observe that their spectral properties are similar.

Then we selected the excitation peak at 378.5 nm as the excitation wavelength to measure the IR luminescence spectrum in the range of 908–1680 nm, as also shown in Fig. 3. We found that the luminescence peaks are positioned at 978.0 and 1532.0 nm. We recognize that these luminescence peaks are respectively the 4I11/2 → 4I15/2 and 4I13/2 → 4I15/2 fluorescence transitions of the Er³⁺ ion [16,18]. We found that the luminescence intensities, when excited by 378.5 nm light, are approximately 3.91 x 10⁵ and 3.38 x 10⁶ for the 4I11/2 → 4I15/2 and 4I13/2 → 4I15/2 luminescence transitions of the sample (A) Er³⁺ (3.2%):tellurium glass. We found also that they are 1.72 x 10⁵ and 1.33 x 10⁶ for the sample (B) Er³⁺ (0.5%):tellurium glass. We calculated that the luminescence intensities of the 978.0 nm 4I11/2 → 4I15/2 and 1532.0 nm 4I13/2 → 4I15/2 transitions of (A) Er³⁺ (3.2%):tellurium glass are respectively 2.27 and 2.55 times larger than those of (B) Er³⁺ (0.5%):tellurium glass. We also selected the excitation peaks at 488.0 and 522.0 nm as the excitation wavelengths to measure the IR luminescence spectra in the range of
and \( \eta \) populate at the ET lifetime curves exhibit an obvious energy transfer phenomenon. Luminescence spectra by a factor of 1.80 exhibiting a concomitant enhancement in the IR excitation and fluorescence spectral intensities decrease by a factor of 0.87 increased from 0.5\% to 3.2\%, the visible excitation and luminescence peak wavelengths. When the concentration of the \( {\text{Er}}^{3+} \) ions is small and can be ignored when \( x = 0.5\% \). Therefore, \( I_{0.5\%\text{Er}} \) can represent the case of nonenergy transfer.

Using Eq. (1), we calculated the integrated summation value for the luminescence lifetime curves shown in Fig. 6. The results of these calculations are as follows: \( \eta_{n,3.2\%\text{Er}}(550.0 \text{ nm}) = 59.9\% \), \( \eta_{n,3.2\%\text{Er}}(522.0 \text{ nm}) = 59.0\% \), \( \eta_{n,3.2\%\text{Er}}(658.0 \text{ nm}) = 38.2\% \), \( \eta_{n,3.2\%\text{Er}}(800.0 \text{ nm}) = 56.7\% \), and \( \eta_{n,5.0\%\text{Er}}(550.0 \text{ nm}) = 76.7\% \), \( \eta_{n,5.0\%\text{Er}}(522.0 \text{ nm}) = 76.7\% \), \( \eta_{n,5.0\%\text{Er}}(658.0 \text{ nm}) = 54.1\% \), \( \eta_{n,5.0\%\text{Er}}(800.0 \text{ nm}) = 74.6\% \).

7. ANALYSIS

From the above measurements and analyses, we can see that the excitation spectra of 1532.0 nm IR light and 550.0 nm visible light are very similar in the shape of the waveform and in the peak wavelengths. When the concentration of the \( {\text{Er}}^{3+} \) ions is increased from 0.5\% to 3.2\%, the visible excitation and luminescence spectral intensities decrease by a factor of 0.87−1.91, exhibiting a concomitant enhancement in the IR excitation and luminescence spectra by a factor of 1.80−5.49. In addition, the lifetime curves exhibit an obvious energy transfer phenomenon. Therefore, we conclude that the behavior observed is the multiphoton near-IR quantum cutting luminescence phenomenon \([1-12,15-17,19-22]\). More careful analyses of the quantum cutting mechanism are presented below. The energy levels of the \( {\text{Er}}^{3+} \) ions and the quantum cutting passage are shown in Fig. 7.

When the \( {4I}_{9/2} \) energy level is excited, many \( {\text{Er}}^{3+} \) ions may populate at the \( {4I}_{9/2} \) energy level because the nonradiative multiphonon relaxation of the \( {4I}_{9/2} \) energy level is small, and the energy gap between the \( {4I}_{9/2} \) and \( {4I}_{11/2} \) energy levels is more than 2000 cm\(^{-1}\), which is obviously larger than the 760 cm\(^{-1}\) phonon energy of tellurium glass. In this case, the \( {\text{Er}}^{3+} \) ion possesses an intense \( {4I}_{9/2} \rightarrow {4I}_{13/2}, {4I}_{15/2} \rightarrow {4I}_{13/2} \) ET\(^{-31} \) − ET\(^{31} \) cross-energy transfer process. Its transition mismatch, \( \Delta E = -682 \text{ cm}^{-1} \), is moderate, but its reduced matrix elements \( \langle U_j^2 \rangle \) (0.0003, 0.0087, 0.7100) and (0.0195, 0.1172, 1.4325) are very large and the multiphonon nonradiative relaxation is small \([16,18]\), so the cross-energy transfer rate of \( {4I}_{9/2} \rightarrow {4I}_{13/2}, {4I}_{15/2} \rightarrow {4I}_{13/2} \) ET\(^{-31} \) − ET\(^{31} \) between the
The Er³⁺ ion also possesses a very intense \( ^{2}H_{11/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{15/2} \rightarrow ^{1}I_{13/2} \) ET\(^{63} \) - ET\(^{01} \) cross-energy transfer process. It can be calculated from the absorption spectrum of Fig. 1 that its transition mismatch, \( \Delta E = 3.4 \text{ cm}^{-1} \), is very small, and the reduced matrix elements \( (U)^{2} \) (0.1953, 0.0648, 0.2837) and (0.0195, 0.1172, 1.4325) are very large [16,18], but its multiphonon nonradiative relaxation is large, so the cross-energy transfer rate of \( ^{2}H_{11/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{15/2} \rightarrow ^{1}I_{13/2} \) ET\(^{63} \) - ET\(^{01} \) is very intense. The population of the \( ^{4}I_{13/2} \) energy level may first be transferred to the first excited state \( ^{4}I_{13/2} \) and the \( ^{4}I_{15/2} \) energy level, mainly through the \( ^{2}H_{11/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{15/2} \rightarrow ^{1}I_{13/2} \) ET\(^{63} \) - ET\(^{01} \) cross-energy transfer process. The population in the \( ^{1}I_{13/2} \) energy level may be sequentially transferred to \( ^{4}I_{13/2} \) via \( ^{4}I_{13/2} \rightarrow ^{1}I_{13/2} \) ET\(^{63} \) - ET\(^{01} \) and \( ^{4}I_{13/2} \rightarrow ^{1}I_{13/2} \) ET\(^{63} \) - ET\(^{01} \). This results in the intense four-photon near-IR quantum cutting of the \( ^{4}I_{13/2} \rightarrow ^{4}I_{15/2} \) luminescence.

The Er³⁺ ion also possesses an intense \( ^{2}H_{11/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{15/2} \rightarrow ^{1}I_{13/2} \) ET\(^{91} \) - ET\(^{05} \) cross-energy transfer process. The population of the \( ^{2}H_{11/2} \) energy level may first be transferred to the first excited state \( ^{4}I_{13/2} \) and the \( ^{4}I_{15/2} \) energy level, and sequentially transferred to \( ^{4}I_{13/2} \) via \( ^{2}H_{11/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{15/2} \rightarrow ^{1}I_{13/2} \) ET\(^{91} \) - ET\(^{05} \) and \( ^{4}I_{15/2} \rightarrow ^{4}I_{13/2} \) ET\(^{91} \) - ET\(^{05} \). This results in the intense four-photon near-IR quantum cutting of the \( ^{4}I_{13/2} \rightarrow ^{4}I_{15/2} \) luminescence.

The Er³⁺ ion also possesses an intense \( ^{2}G_{11/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{15/2} \rightarrow ^{2}G_{11/2} \) ET\(^{101} \) - ET\(^{06} \) cross-energy transfer process. The population of the \( ^{2}G_{11/2} \) energy level may first be transferred to the first excited state \( ^{4}I_{13/2} \) and the \( ^{4}I_{15/2} \) energy level, and sequentially transferred to \( ^{4}I_{13/2} \) via \( ^{2}G_{11/2} \rightarrow ^{4}I_{13/2}, ^{4}I_{15/2} \rightarrow ^{2}G_{11/2} \) ET\(^{101} \) - ET\(^{06} \) and \( ^{4}I_{15/2} \rightarrow ^{4}I_{13/2} \) ET\(^{101} \) - ET\(^{06} \). This results in the intense four-photon near-IR quantum cutting of the \( ^{4}I_{13/2} \rightarrow ^{4}I_{15/2} \) luminescence.

The Er³⁺ ion possesses an intense \( ^{4}G_{9/2} \rightarrow ^{4}F_{2/2}, ^{4}I_{15/2} \rightarrow ^{1}I_{13/2} \) ET\(^{117} \) - ET\(^{01} \) cross-energy transfer process. The population of the \( ^{4}G_{9/2} \) energy level may be first transferred to the first excited state \( ^{4}I_{13/2} \) and the \( ^{4}F_{2/2} \) energy level, and sequentially transferred to \( ^{4}I_{13/2} \) via \( ^{4}G_{9/2} \rightarrow ^{4}F_{2/2}, ^{4}I_{15/2} \rightarrow ^{1}I_{13/2} \) ET\(^{117} \) - ET\(^{01} \) and \( ^{4}I_{15/2} \rightarrow ^{4}I_{13/2} \) ET\(^{117} \) - ET\(^{01} \). This results in the intense three-photon near-IR quantum cutting of the \( ^{4}I_{13/2} \rightarrow ^{4}I_{15/2} \) luminescence.

Fig. 7. Schematic diagram of the energy levels of the Er³⁺ ion and the quantum cutting passage.
In Eq. (2a), the original and the theoretical up-limits of the efficiency of other cross-energy transfers when the energy level is excited can be expressed by the following equations:

\[
\eta_{\text{CR,}\times\text{Er}}(\mathcal{S}_{3/2}) = \eta_{S_{3/2}}[1 - \eta_{\text{tr,Er}}(\mathcal{S}_{3/2})]
\]

\[
+ \{(1 - \eta_{I_{15/2}})\eta_{\text{lower}}[1 - \eta_{\text{tr,Er}}(\mathcal{S}_{3/2})]
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{S}_{3/2})\{\eta_{\text{CR,Er}}(\mathcal{I}_{15/2})\}
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{S}_{3/2})
\]

\[
(4a)
\]

\[
\eta_{\text{CR,}\times\text{Er}}(\mathcal{S}_{3/2}) = \eta_{S_{3/2}}[1 - \eta_{\text{tr,Er}}(\mathcal{S}_{3/2})]
\]

\[
+ \{(1 - \eta_{I_{15/2}})\eta_{\text{lower}}[1 - \eta_{\text{tr,Er}}(\mathcal{S}_{3/2})]
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{S}_{3/2})\{\eta_{\text{CR,Er}}(\mathcal{I}_{15/2})\}
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{S}_{3/2})
\]

\[
(4b)
\]

The original and the theoretical up-limits of the efficiency of the three-photon near-IR quantum cutting of the Er\(^{3+}\) ion induced by \{\(\mathcal{H}_{11/2} \rightarrow \mathcal{I}_{15/2} \rightarrow \mathcal{I}_{15/2}\)\} \text{ET}^{53} \rightarrow \text{ET}^{51} and other cross-energy transfers when the \(\mathcal{I}_{15/2}\) energy state is excited can be expressed by the following equations:

\[
\eta_{\text{CR,}\times\text{Er}}(\mathcal{H}_{11/2}) = \eta_{\text{H}_{11/2}}[1 - \eta_{\text{tr,Er}}(\mathcal{H}_{11/2})]
\]

\[
+ \{(1 - \eta_{I_{15/2}})\eta_{\text{lower}}[1 - \eta_{\text{tr,Er}}(\mathcal{H}_{11/2})]
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{H}_{11/2})\{\eta_{\text{CR,Er}}(\mathcal{I}_{15/2})\}
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{H}_{11/2})
\]

\[
(5a)
\]

\[
\eta_{\text{CR,}\times\text{Er}}(\mathcal{H}_{11/2}) = \eta_{\text{H}_{11/2}}[1 - \eta_{\text{tr,Er}}(\mathcal{H}_{11/2})]
\]

\[
+ \{(1 - \eta_{I_{15/2}})\eta_{\text{lower}}[1 - \eta_{\text{tr,Er}}(\mathcal{H}_{11/2})]
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{H}_{11/2})\{\eta_{\text{CR,Er}}(\mathcal{I}_{15/2})\}
\]

\[
+ \eta_{I_{15/2}}\eta_{\text{tr,Er}}(\mathcal{H}_{11/2})
\]

\[
(5b)
\]

Using Eqs. (2)–(5) and the data regarding cross-energy transfer efficiency, we can easily calculate that \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{I}_{15/2})_{\text{UL}} = 157\%\), \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{F}_{9/2})_{\text{UL}} = 138\%\), \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{S}_{3/2})_{\text{UL}} = 193\%\), and \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{H}_{11/2})_{\text{UL}} = 192\%\), and that \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{I}_{15/2})_{\text{UL}} = 175\%\), \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{F}_{9/2})_{\text{UL}} = 154\%\), \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{S}_{3/2})_{\text{UL}} = 233\%\), and \(\eta_{\text{CR,}\times\text{Er}}(\mathcal{H}_{11/2})_{\text{UL}} = 233\%\). These analyses of the quantum cutting mechanism and its efficiency are in agreement with the experimental results.

8. CONCLUSION

In the present work, we measured the absorption spectrum and the excitation and luminescence spectra, as well as the lifetime dynamics of Er\(^{3+}\)-doped tellurium glass. We found that the excitation spectra of 1532.0 nm IR light and 550.0 nm visible light are very similar in the shape of the waveform and in the peak wavelengths. When the concentration of Er\(^{3+}\) ions was increased from 0.5% to 3.2%, the visible excitation and luminescence spectral intensities decreased by a factor of 0.87–1.91, with a concomitant enhancement in the IR excitation and luminescence spectra by a factor of 1.80–5.49. In addition, the lifetime curves exhibited an obvious energy transfer phenomenon. Therefore, we concluded that the present phenomenon is the multiphoton near-IR quantum cutting luminescence phenomenon. We then calculated the cross-energy transfer efficiency from the measured lifetimes of samples (A) Er\(^{3+}\) (3.2%): tellurium glass, (B) Er\(^{3+}\) (0.5%): tellurium glass, and (C) Er\(^{3+}\) (5.0%): tellurium glass. We carefully analyzed the mechanisms behind these near-IR quantum cutting behaviors. We found that there is two-photon, two-photon, three-photon, two-photon, three-photon, four-photon, four-photon, and three-photon quantum cutting when
the $^{4}I_{9/2}$, $^{4}F_{3/2}$, $^{4}S_{3/2}$, $^{2}H_{11/2}$, $^{4}F_{7/2}$, $^{4}F_{5/2}$, $^{2}H_{9/2}$, and $^{4}G_{9/2}$ energy levels, respectively, are excited by 800.0, 652.0, 543.0, 520.5, 488.5, 450.5, 406.5, 378.0, and 365.5 nm light. From the measured experimental results, we found that the up-limits of the near-IR quantum cutting efficiency of the $^{4}I_{9/2}$, $^{4}F_{3/2}$, $^{4}S_{3/2}$, and $^{2}H_{11/2}$ states are respectively 157%, 138%, 193%, and 192% for (A) $^{3+}$ (3.2%): tellurium glass. We found also that they are 175%, 154%, 233%, and 233% for (C) $^{3+}$ (5.0%): tellurium glass. These measured results are useful for the next generation of environmentally friendly Ge and a-Si solar cells, a current and globally important area of research.

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**REFERENCES**


