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Spectroscopic properties and energy transfer processes in Er\textsuperscript{3+}/Nd\textsuperscript{3+} co-doped tellurite glass for 2.7-µm laser materials

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Intense 2.7-µm emissions are obtained from Er\textsuperscript{3+}/Nd\textsuperscript{3+} co-doped tellurite glass samples under the 808-nm laser diode excitation. According to the absorption spectra, Judd-Oelft parameters and radiative transition probabilities are calculated and analyzed using the Judd-Oelft theory. The spectroscopic properties and energy transfer mechanism between Er\textsuperscript{3+} and Nd\textsuperscript{3+} are analyzed. The effects of OH\textsuperscript{−} content on the spectroscopic properties of Er\textsuperscript{3+}/Nd\textsuperscript{3+} co-doped samples are discussed. The obtained results indicate that Er\textsuperscript{3+}/Nd\textsuperscript{3+} co-doped tellurite glass can significantly develop optical properties of 2.7-µm emission, if OH\textsuperscript{−} groups can be effectively eliminated.

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method on those equations, the J-O intensity parameter strengths. By employing the least square fitting procedures, the absorption spectrum. A set of equations, depending on the number of absorption bands considered for the simulation, was generated from the measured electric dipole line strength. Employing the least square fitting method on those equations, the J-O intensity parameters $\Omega_t$ ($t = 2, 4, 6$) were attained. The parameters were $\Omega_2 = 9.68 \times 10^{-20}$ cm$^2$, $\Omega_4 = 1.11 \times 10^{-20}$ cm$^2$, and $\Omega_6 = 1.89 \times 10^{-20}$ cm$^2$, respectively, which were similar to those in tellurite systems reported before$^{[27]}$. The root-mean-square error deviation of the calculated and experimental transition oscillator strength was $0.7 \times 10^{-6}$, which was close to that of other reported types of glass$^{[28]}$. The results verified the reliability of the calculations as well as the validity of the Judd-Ofelt theory for the spectral intensities of Er$^{3+}$ ions.

In general, radiative properties can be predicted by intensity parameters $\Omega_t$. The line strength for an electric-dipole transition ($S_{ed}$) can be given by$^{[29]}

$$S_{ed} = \sum_{t=2,4,6} \Omega_t |4f^N(S, L) J || U(t) || 4f^N(S', L') J'||^2.$$

(1)

Additionally, the line strength for a magnetic-dipole transition ($S_{md}$) between $J$ manifolds when the transitions subject to the selection rules ($\Delta S=\Delta L=0$; $\Delta J=\pm 1$ or 0) are represented as

$$S_{md} = \frac{1}{4m_e^2e^2} |(S, L) J || L + 2S || (S', L') J'||^2. \quad (2)$$

Subsequently, the spontaneous transition probabilities are given by

$$A[(S, L) J; (S', L') J'] = A_{ed} + A_{md} \quad (3)$$

$$= \frac{64\pi^4e^2}{3h\lambda^2(2J+1)} \times \left[ \frac{n(n^2+2)^2}{9} S_{ed} + n^3S_{md} \right].$$

where $A_{ed}$ and $A_{md}$ are the electric-dipole transition and magnetic-dipole spontaneous transition probability, respectively.

Furthermore, the fluorescence branching ratios $\beta$ and radiative lifetimes $\tau_{rad}$ can be calculated from

$$\beta[(S, L) J; (S', L') J'] = \frac{A[(S, L) J; (S', L') J']}{\sum_{S', L', J'} A[(S, L) J; (S', L') J']},$$

$$\tau_{rad} = \left\{ \sum_{S', L', J'} A[(S, L) J; (S', L') J'] \right\}^{-1}. \quad (5)$$

Using Eqs. (1)–(5) and $\Omega_t$ parameters, the spontaneous transition probability ($A$), total spontaneous transition probability ($\sum A$), radiative lifetime ($\tau_{rad}$), and branching ratios ($\beta$) of the optical transitions for the Er$^{3+}$ doped tellurite glass were calculated (Table 1). The predicted spontaneous emission probabilities for $^{4}\text{I}_{11/2} \rightarrow ^{4}\text{I}_{13/2}$ of Er$^{3+}$ was 79.54 s$^{-1}$, which was higher than those of fluorophosphates (22.16 s$^{-1}$). A higher spontaneous emission probability generally provides a better opportunity to obtain laser operation. Therefore, the tellurite glass in this work can be a promising host material to achieve 2.7-$\mu$m emission based on the Er$^{3+}$:$^{4}\text{I}_{11/2} \rightarrow ^{4}\text{I}_{13/2}$ transition.

Once the J-O Parameters are known, the radiative properties can be calculated, such as the radiative transition probabilities ($A$) and branching ratio of the $^{4}\text{I}_{11/2} \rightarrow ^{4}\text{I}_{13/2}$ transition ($\beta$), which are also shown in Table 1. The radiative transition rate A and fluorescence.

**Table 1. Predicted Spontaneous Transition Probability ($A$), Total Spontaneous Transition Probability ($\sum A$), Branching Ratios ($\beta$), and Radiative Lifetimes ($\tau$) of Tellurite Glass for Various Selected Excited Levels of Er$^{3+}$**

<table>
<thead>
<tr>
<th>Transition</th>
<th>$A$ (s$^{-1}$)</th>
<th>$\sum A$ (s$^{-1}$)</th>
<th>$\beta$ (%)</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{4}\text{I}<em>{13/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>422.01</td>
<td>422.01</td>
<td>100.00</td>
<td>2.37</td>
</tr>
<tr>
<td>$^{4}\text{I}<em>{11/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>502.47</td>
<td>582.01</td>
<td>86.33</td>
<td>1.72</td>
</tr>
<tr>
<td>$^{4}\text{I}_{13/2}$</td>
<td>79.54</td>
<td></td>
<td>13.67</td>
<td></td>
</tr>
<tr>
<td>$^{4}\text{I}<em>{9/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>188.69</td>
<td>338.23</td>
<td>55.79</td>
<td>2.96</td>
</tr>
<tr>
<td>$^{4}\text{I}_{13/2}$</td>
<td>144.92</td>
<td></td>
<td>42.85</td>
<td></td>
</tr>
<tr>
<td>$^{4}\text{I}_{11/2}$</td>
<td>6.2</td>
<td></td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>$^{4}\text{F}<em>{9/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>3027.23</td>
<td>3426.76</td>
<td>88.34</td>
<td>0.29</td>
</tr>
<tr>
<td>$^{4}\text{I}_{13/2}$</td>
<td>164.20</td>
<td></td>
<td>4.79</td>
<td></td>
</tr>
<tr>
<td>$^{4}\text{I}_{11/2}$</td>
<td>223.20</td>
<td></td>
<td>6.51</td>
<td></td>
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<tr>
<td>$^{4}\text{I}_{9/2}$</td>
<td>12.13</td>
<td></td>
<td>0.35</td>
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<td>$^{4}\text{S}<em>{3/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>1688.30</td>
<td>5826.39</td>
<td>63.37</td>
<td>0.17</td>
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<tr>
<td>$^{4}\text{I}_{13/2}$</td>
<td>111.84</td>
<td></td>
<td>1.92</td>
<td></td>
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<tr>
<td>$^{4}\text{I}_{11/2}$</td>
<td>153.99</td>
<td></td>
<td>2.64</td>
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<tr>
<td>$^{2}\text{H}<em>{11/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>2445.45</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$^{4}\text{F}<em>{7/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>8058.62</td>
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<tr>
<td>$^{4}\text{F}<em>{5/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
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<tr>
<td>$^{2}\text{H}<em>{9/2} \rightarrow ^{4}\text{I}</em>{15/2}$</td>
<td>3377.32</td>
<td>10582.77</td>
<td>0.01</td>
<td>0.09</td>
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<td>$^{4}\text{I}_{13/2}$</td>
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<td></td>
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</tr>
<tr>
<td>$^{4}\text{I}_{11/2}$</td>
<td>1723.11</td>
<td></td>
<td>16.28</td>
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</table>

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branch ratio $\beta$ of $^{4}I_{11/2}$ to $^{4}I_{13/2}$ of Er$^{3+}$ were 79.54 s$^{-1}$ and 13.67%, respectively.

Figure 2(b) shows the 1.5-µm emission spectra pumped by 808 nm. The emission around 1.5-µm was observed as due to the transition of Er$^{3+}$: $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$. With the increase of the Nd$^{3+}$ doping concentration, 1.5-µm emission intensity decreased obviously. The emission intensity decreased with the further increase of the Nd$^{3+}$ concentration. The same phenomenon can also be observed in Fig. 2(a).

Figure 2(c) shows 2.7-µm emission spectra pumped by 808 nm: the Er$^{3+}$ doped sample is shown to have almost no emission around 2.7 µm. With the increase of the Nd$^{3+}$ concentration, the intensity of the emission at 2.7 µm increased gradually.

Without Nd$^{3+}$ as sensitizer, the Er$^{3+}$-doped glass presented the very weak intensity of 2.7-µm emission spectra, compared with the strong 550-nm and 1.5-µm emissions. The increase in the content of Nd$^{3+}$ not only led to an enhancement in the 2.7-µm emission but also in the reduction in the 550-nm and 1.5-µm optical emissions, as shown in Fig. 3. As a consequence, Nd$^{3+}$ may be concluded as a suitable sensitizer to enhance the 2.7-µm emission in Er$^{3+}$-doped tellurite glass. Nd$^{3+}$ ions can obviously enhance the absorption of the pump energy and transfer the energy to Er$^{3+}$ ions. Meanwhile, they could be the quenching center for the 550-nm up-conversion and 1.5-µm emission.

According to the abovementioned absorption and emission spectra, the physical mechanism describing both visible and infrared emissions can be summarized as shown in Fig. 3. Er$^{3+}$ ions were first excited from the ground state to the $^{4}I_{9/2}$ level by an 808-nm laser. Meanwhile, Nd$^{3+}$ ions were excited directly to the $^{5}F_{5/2}$ and $^{2}H_{9/2}$ levels. On one hand, a part of the excited Nd$^{3+}$ ions relaxed non-radiatively to the $^{4}F_{3/2}$ level. On the other hand, Nd$^{3+}$ ions in the $^{4}F_{5/2}$, $^{2}H_{9/2}$, and $^{4}F_{3/2}$ levels transferred their energy to Er$^{3+}$: $^{4}I_{9/2}$ and $^{4}I_{11/2}$ via the processes (Nd$^{3+}$: $^{4}F_{5/2}$, $^{2}H_{9/2}$ + Er$^{3+}$: $^{4}I_{15/2}$) $\rightarrow$ (Nd$^{3+}$: $^{4}I_{9/2}$ + Er$^{3+}$: $^{4}I_{15/2}$), (Nd$^{3+}$: $^{4}F_{5/2}$, $^{2}H_{9/2}$ + Er$^{3+}$: $^{4}I_{15/2}$) $\rightarrow$ (Nd$^{3+}$: $^{4}I_{9/2}$ + Er$^{3+}$: $^{4}I_{15/2}$), and (Nd$^{3+}$: $^{4}F_{5/2}$ + Er$^{3+}$: $^{4}I_{15/2}$) $\rightarrow$ (Nd$^{3+}$: $^{4}I_{9/2}$ + Er$^{3+}$: $^{4}I_{11/2}$). These energy transfer processes increased the population of Er$^{3+}$: $^{4}I_{11/2}$, which led to enhanced 2.7-µm emission corresponding to $^{4}I_{11/2} \rightarrow ^{4}I_{13/2}$. As a result, the increasing population of Er$^{3+}$: $^{4}I_{13/2}$ could lead to an increasing 550-nm up-conversion and 1.5-µm emission. However, an obvious decrease was observed in the 550-nm and 1.5-µm emissions, which may be due to the presence of energy transfer channels, such as the following: (Er$^{3+}$: $^{4}I_{13/2}$ + Nd$^{3+}$: $^{4}I_{9/2}$) $\rightarrow$ (Er$^{3+}$: $^{4}I_{15/2}$ + Nd$^{3+}$: $^{4}I_{15/2}$) or/and (Er$^{3+}$: $^{4}I_{13/2}$ + Nd$^{3+}$: $^{4}I_{15/2}$) $\rightarrow$ (Er$^{3+}$: $^{4}I_{15/2}$ + Nd$^{3+}$: $^{4}F_{5/2}$, $^{2}H_{9/2}$). Therefore, the population of Er$^{3+}$: $^{4}I_{13/2}$ decreased, which led to a reduction in both 550-nm up-conversion and 1.5-µm emission.

In general, the introduction of OH$^{-}$ groups in oxide types of glass prepared in air atmosphere cannot be avoided. OH$^{-}$ content can be determined by the IR spectra. Figure 4 shows the IR spectra of 1 mol% Er$^{3+}$ and 2 mol% Nd$^{3+}$ doped samples with and without 60 min of bubbling. The samples showed a broad, strong absorption at 4.35 and 3.33 µm without bubbling. Absorption bands are commonly attributed to the stretching vibration of OH$^{-}$ groups. Previous studies showed that the absorption band at 3.33 µm is due to free OH$^{-}$ groups, while the band at 4.35 µm is attributed to hydrogen-bonded OH$^{-}$ groups. Thus, the OH$^{-}$ content in the sample without bubbling oxygen was larger than that in the
samples with bubbling.

The maximum transmittance reached as high as 75%. The 25% loss covered the Fresnel reflections, dispersion, and absorption of the glass. The \( \text{OH}^- \) groups contained in the glass can be expressed by the absorption coefficient of the \( \text{OH}^- \) vibration band at 3.33 \( \mu \text{m} \), given by\(^{[30]}\)

\[
\alpha = \ln(T_o/T)/l,
\]

where \( l \) is the thickness of a sample, and \( T_o \) and \( T \) are the transmitted intensity and incident intensity, respectively. The absorption coefficient of the sample with bubbling \( \alpha \) at 3.33 \( \mu \text{m} \) was 0.979 \( \text{cm}^{-1} \), lower than that without 60 min of bubbling. After bubbling in oxygen, the sample presented better IR transmission property.

According to Ref. \(^{[31]}\), the content of the free \( \text{OH}^- \) groups in glass can be estimated from the measured absorption coefficient at 3.33 \( \mu \text{m} \). The free \( \text{OH}^- \) group \( N_{\text{OH}} \) (ions/cm\(^3\)) can be obtained by

\[
N_{\text{OH}} = \frac{N}{\varepsilon \cdot L \ln \frac{1}{T}},
\]

where \( N \) is the Avogadro constant, \( L \) is the thickness of glass, \( T \) is the transmittance, and \( \varepsilon \) is the molar absorptivity of the free \( \text{OH}^- \) groups in glass. The present study adopted the molar absorptivity \( \varepsilon \) of the free \( \text{OH}^- \) groups in silicate glass, 49.1 \( \times 10^3 \) cm\(^2\)/mol\(^{[32]}\), given the lack of relevant reports on tellurite glass. Thus, the \( \text{OH}^- \) concentration in the sample with bubbling was estimated as \( N_{\text{OH}} = 4.73 \times 10^{19} \text{cm}^{-3} \), an obvious reduction compared with the sample without bubbling (\( N_{\text{OH}} = 6.89 \times 10^{19} \text{cm}^{-3} \)).

Free \( \text{OH}^- \) is one of the dominant quenching centers in \( \text{Er}^{3+}/\text{Nd}^{3+} \) co-doped glass specimens. According to Ref. \(^{[33]}\), two possible energy-transfer mechanisms exist between \( \text{Er}^{3+} \) ions and free \( \text{OH}^- \) groups in glass: 1) a small fraction of excited \( \text{Er}^{3+} \) ions closely bound to free \( \text{OH}^- \) groups can be quenched rapidly; 2) other excited \( \text{Er}^{3+} \) ions can transfer the excitation to neighboring non-excited \( \text{Er}^{3+} \) ions in the first few steps and finally be quenched by free \( \text{OH}^- \) groups in the transfer route. The latter mechanism should be dominant because most of the excited \( \text{Er}^{3+} \) ions are not bound with free \( \text{OH}^- \) groups closely. Therefore, when either the concentration of \( \text{Er}^{3+} \) ions or the content of free \( \text{OH}^- \) groups is high enough, the possibility of energy transfer between excited \( \text{Er}^{3+} \) ions and free \( \text{OH}^- \) groups can become high; the quenching behavior can then become significant.

According to the considerations of non-radiative processes, the total rate is \( 1/\tau_m \), which is given by\(^{[34]}\)

\[
\frac{1}{\tau_m} = A_{\text{rad}} + W_{\text{OH}} + W_{\text{mp}},
\]

where \( A_{\text{rad}} \) is the radiative decay rate, equal to the reciprocal of the decay rate in the absence of \( \text{OH}^- \) groups. \( W_{\text{mp}} \) is the multiphonon decay rate, and \( W_{\text{OH}} \) is the energy transfer rate between \( \text{Er}^{3+} \) and \( \text{OH}^- \). The multiphonon relaxation can be considered negligible (<1 s\(^{-1}\)) for tellurite glass, which processes relative low phonon energy (700 cm\(^{-1}\)). The energy transfer rate between

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{2.7-\( \mu \text{m} \) emission spectra of 1-mol\% \( \text{Er}^{3+} \) and 2-mol\% \( \text{Nd}^{3+} \) doped samples with and without 60 min of bubbling.}
\end{figure}

\( \text{Er}^{3+} \) ions and \( \text{OH}^- \) groups, \( W_{\text{OH}} \), is proportional to the acceptor and donor concentration, and given by

\[
W_{\text{OH}} = K_{\text{OH-Er}} N_{\text{Er}} N_{\text{OH}},
\]

where \( K_{\text{OH-Er}} \) is a constant, as determined by the strength of interactions between \( \text{Er}^{3+} \) ions and \( \text{OH}^- \) groups in the case of energy transfer, independent of the concentrations of \( \text{Er}^{3+} \) and \( \text{OH}^- \). \( N_{\text{Er}} \) is the \( \text{Er}^{3+} \) concentration (donor concentration), which is a constant in this paper, and \( N_{\text{OH}} \) is the concentration of the \( \text{OH}^- \) groups.

According to Eqs. (8) and (9), while at a high \( \text{OH}^- \) groups concentration, the energy transfer rate between \( \text{Er}^{3+} \) and \( \text{OH}^- \) would be higher, which leads to a reduction of the lifetime (\( \tau_m \)) for the \( ^{4}I_{11/2} \) level of \( \text{Er}^{3+} \) in the sample.

Moreover, the 2.7-\( \mu \text{m} \) emission intensity of \( \text{Er}^{3+}/\text{Nd}^{3+} \) co-doped tellurite glass samples with 60 min of bubbling is higher than that without bubbling, as seen in Fig. 5. This result indicates the necessity to remove \( \text{OH}^- \) groups in the preparation process in order to obtain intense 2.7-\( \mu \text{m} \) emission.

In conclusion, intense emission at 2.7 \( \mu \text{m} \) is obtained in the \( \text{Er}^{3+}/\text{Nd}^{3+} \) co-doped tellurite glass samples. An enhanced absorption of the 808-nm pumping light with the increasing content of \( \text{Nd}^{3+} \) is observed. The increasing component of \( \text{Nd}^{3+} \) not only leads to an enhancement in the 2.7-\( \mu \text{m} \) emission but also in a reduction in the 550-nm and 1.5-\( \mu \text{m} \) emissions. The energy transfer mechanisms between \( \text{Nd}^{3+} \) and \( \text{Er}^{3+} \) are discussed. The \( \text{OH}^- \) groups have influences on the IR and the emission spectra. The results prove that the introducing \( \text{Nd}^{3+} \) to host glass specimens and removing \( \text{OH}^- \) groups in the preparation process can greatly improve the 2.7-\( \mu \text{m} \) emission as well as decrease the 550-nm up-conversion and 1.5-\( \mu \text{m} \) emission.

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