

Indirect excitation of Er^{3+} in sol-gel hybrid films doped with an erbium complex

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Transparent sol-gel hybrid films doped with erbium tris 8-hydroxyquinoline were prepared using methyltriethoxysilane, vinyltriethoxysilane, and phenyltrimethoxysilane as precursors. We obtain a strong $1.53\text{-}\mu\text{m}$ Er^{3+} luminescence with a wide full width at half-maximum and no thermal quenching. Comparison of absorption of the film with the pump wavelength dependence of Er^{3+} luminescence intensity indicates the presence of an efficient indirect excitation path for Er^{3+} via organic ligands. © 2003 American Institute of Physics. [DOI: 10.1063/1.1570919]

Erbium-doped materials have attracted considerable attention due to their applications in optical telecommunications. Since erbium-doped fiber amplifiers (EDFAs) appeared in 1987, they have been used as repeaters, post or preamplifiers, and power amplifiers in long distance optical transmission systems. However, their bulky nature and extremely high price are obstacles to EDFAs being widely employed in access networks. Although low-cost planar-type optical amplifiers have been the subject of much study, they still employ waveguides with an expensive, high-power laser diode resonantly pumping one of the Er^{3+} absorption bands.^{1,2} Thus, it is necessary to develop an Er-doped system that can be pumped with a low-cost pump source. Recently, the indirectly excitable Er-doped system has received extensive attention. This system allows pumping of Er^{3+} by using "sensitizers" that absorb pump energy and transfer it to the Er^{3+} ions. Si nanoclusters and the organic ligands of Er complex have been successfully used as sensitizers.³⁻⁵

Sol-gel hybrid (SGH) materials composed of both inorganic and organic components enable both inorganic and organic dopants to be incorporated with relatively high thermal stability. Therefore, SGH materials are potential candidates for planar optical amplifiers. Thus far, SGH materials have been widely studied with a view to their use as passive optical waveguide devices.⁶ However, developing active optical waveguide devices using SGH materials are required for development of a SG based planar waveguide circuits. While there have been a few reports of SGH materials for $1.5\text{-}\mu\text{m}$ amplification, they still use the 980-nm pump source and show a very weak Er^{3+} luminescence at room temperature due to the low absorption and emission cross section of Er^{3+} as well as some quenching effects.⁷ In this letter, we doped an Er complex into SGH materials to improve the luminescence efficiency by increasing the absorption cross section through the indirect excitation of the Er complex. Firstly, we fabricate the SGH material doped with an Er complex. We

then measure $1.5\text{-}\mu\text{m}$ photoluminescence (PL) with different pump wavelengths of an Ar^+ laser, thus demonstrating indirect excitation.

Transparent SGH films were prepared using phenyltrimethoxysilane (Aldrich), vinyltriethoxysilane (Aldrich), and methyltriethoxysilane (Aldrich) as precursors for a SG process. Phenyl, vinyl, and methyl groups were selected for the compatibility with an aromatic Er complex, the increase of network connectivity, and hydrophobic characteristics, respectively. All the precursors were hydrolyzed with 0.01-M HCl solution. A small amount of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DIAMO, Aldrich) was added into the hydrolyzed solution to ensure complete silica condensation. Among several Er complexes, erbium tris 8-hydroxyquinoline (ErQ, Gelest Inc.) was selected due to its bulky aromatic ligand. ErQ was originally synthesized for use in organic light-emitting diodes and shows $1.5\text{-}\mu\text{m}$ PL at room temperature.⁸ However, it shows very low solubility in general organic solvents and hence it was dissolved in acidic solution. The dissolved ErQ solution was mixed with the hybrid solution. The Er/Si ratio was adjusted 5 mol%. This solution was then dripped onto a silicon wafer substrate spinning 1000 rpm. The films were obtained after UV illumination for 1 h and heat-treatment at $150\text{ }^\circ\text{C}$ for 5 h.

The PL spectra of the SGH films doped with ErQ were obtained using an Ar^+ laser, a grating monochromator, and a thermoelectrically cooled InGaAs photodetector. A low noise current preamplifier and a general lock-in technique were used for PL signal amplification. PL excitation (PLE) measurements were also made using the 458-, 477-, 488-, 497-, and 515-nm lines of the Ar^+ laser with the same pump power of 30 mW. A He-cycled cryostat was used for the low-temperature PL measurements.

Figure 1 shows room-temperature PL spectra of the SGH films doped with ErQ. As shown in Fig. 1, the SGH film doped with ErQ gives a clear and broad PL spectra when it is excited using the 477-nm line of the Ar^+ laser with a pump power of 70 mW, even though the 477-nm pump beam is not

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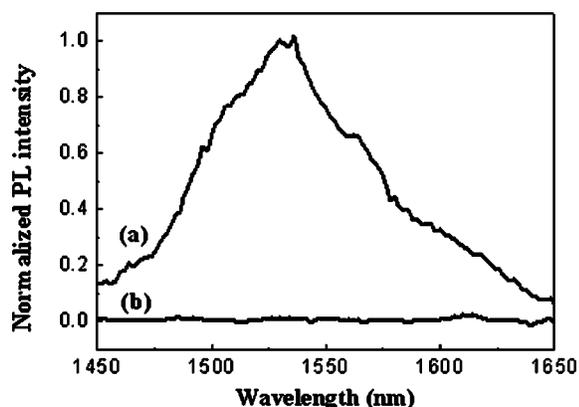


FIG. 1. PL spectra of the SGH film doped with ErQ over infrared wavelengths excited by using (a) 477 and (b) 980 nm, respectively.

absorbed by Er^{3+} ions, indicating that Er^{3+} ions are excited indirectly via the ligands. The main luminescence peak is located at 1532 nm and its full width at half-maximum (FWHM) is about 73 nm. This FWHM is wider than those of other Er complex-doped polymers.⁵ The wide bandwidth indicates that Er^{3+} ions have different local environments in the SGH matrix, which enables a wide gain bandwidth for the optical amplification. Also shown for comparison is the PL spectrum excited by a 980-nm laser diode at the same pump power. We do not observe any Er^{3+} luminescence peak, even though the 980-nm pump beam is resonant with $^4I_{15/2} \rightarrow ^4I_{13/2}$ Er^{3+} absorption band, demonstrating the efficiency of indirect excitation of Er^{3+} . The low PL intensity of

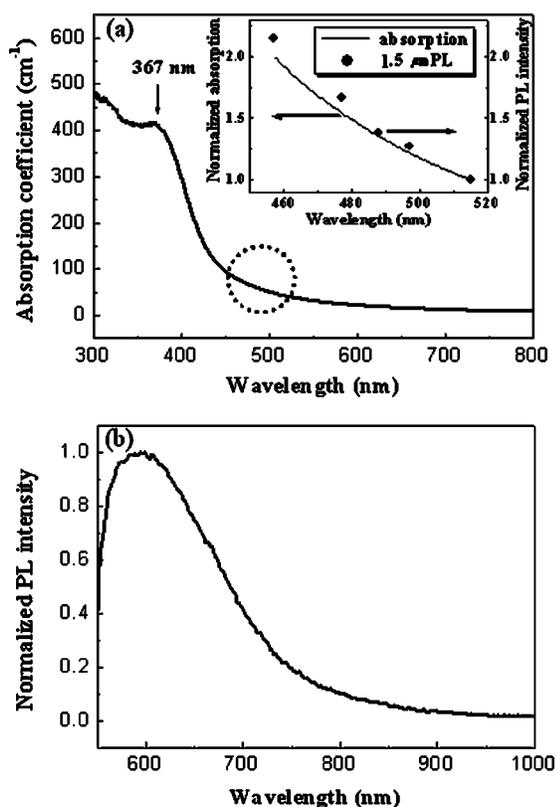


FIG. 2. (a) UV/Vis absorption spectrum of the SGH film doped with ErQ. The inset shows normalized absorption and 1.5- μm PL intensity of the SGH film doped with ErQ as a function of excitation wavelength. (b) Normalized PL spectrum of the SGH film doped with ErQ over visible wavelengths.

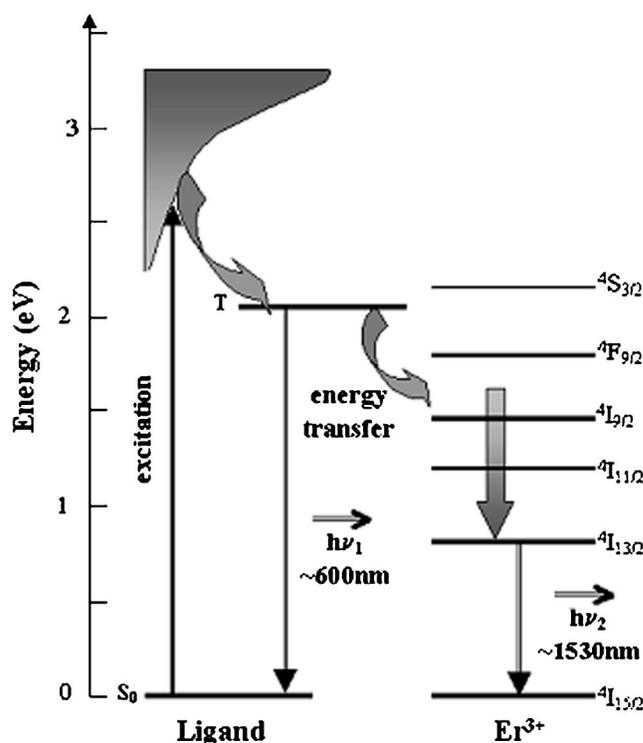


FIG. 3. Schematic energy diagram for the indirect excitation mechanism in the PL of the SGH film doped with ErQ.

Er^{3+} is expected due to a low active fraction when it is pumped at 980 nm.

Figure 2(a) shows the absorption of the SGH film doped with ErQ. The SGH film doped with ErQ shows a broad absorption spectrum that has a maximum in its spectrum at 367 nm, as shown in Fig. 2(a), in agreement with previous reports of ErQ.⁸ The energy difference between the excited state and the ground state of the ligand is estimated to be about 3.5 eV.

To confirm the indirect excitation of Er^{3+} luminescence, the Er^{3+} PL intensities obtained using various lines of an Ar^+ laser with the pump power of 30 mW were compared with optical absorption of the film, as is shown in the inset of Fig. 2. We obtain a good correlation between the absorption and Er^{3+} luminescence without any peaks at 488 or 515 nm, which indicates that the excitation of Er^{3+} is dominated by absorption of the pump beam by ErQ.

Figure 2(b) shows the PL spectrum of the film in the visible range. We observe a peak near 600 nm. This is in agreement with previous results,⁸ and is attributed to triplet-state luminescence of the ligand that is excited via intersystem crossing of the absorbed pump energy. This triplet state, however, can also excite Er^{3+} via exchange interaction.⁹ Thus, we propose a model for the indirect excitation mechanism in the hybrid films doped with ErQ, shown as a schematic energy diagram in Fig. 3. The hydroxyquinoline ligand of ErQ is excited to the band tail state by absorbing the pump energy. The energy of the excited band tail state is then transferred to the triplet excited state of the ligand through intersystem crossing. This triplet state then transfers the energy intramolecularly to Er^{3+} ions. Therefore, when shorter wavelength light is used as an excitation source, more intense

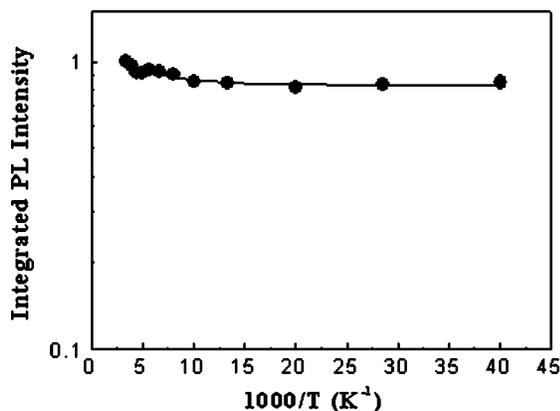


FIG. 4. Integrated Er^{3+} PL intensity of the SGH film doped ErQ as a function of temperature.

Er^{3+} PL can be obtained because the absorption cross section of the ligand increases.

For such indirect Er^{3+} excitation process, when the energy difference between the triplet state and Er^{3+} excited one is too small, the energy can back-transfer from erbium to triplet state of the ligand. For bulk Si, this back-transfer mechanism is known to severely reduce the efficiency of Er^{3+} luminescence at room temperatures,¹⁰ and some temperature quenching has been reported from Er complexed polymers as well.⁵ In the case of the SGH film doped with ErQ, however, no such temperature quenching is expected due to the large mismatch between the triplet state and $^4\text{I}_{13/2}$ state. This is confirmed in Fig. 4, which shows the integrated Er^{3+} PL intensity of the SGH film doped with ErQ in the range of 35 to 300 K. We do not observe any quenching, and the integrated PL intensity indeed slightly

increases with increasing temperature. This result confirms the advantage of using SGH materials for Er doping.

In conclusion, we have demonstrated an efficient Er^{3+} luminescence from the indirect excitation of sol-gel hybrid films doped with ErQ, mediated by the sensitizing effect of the hydroxyquinoline ligand in ErQ. The Er^{3+} luminescence is broad with FWHM of 73 nm. We suggest a model of the indirect excitation in the SGH films doped with ErQ. The SGH films doped with ErQ shows no thermal quenching of Er^{3+} luminescence. Therefore, the SGH films doped with ErQ can be a good candidate for the planar optical amplifiers.

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