Infrared fluorescence and optical gain characteristics of chalcogenide-bound erbium cluster-fluoropolymer nanocomposites

G. A. Kumar and R. E. Riman[a)]
*Department of Materials Science and Engineering, Rutgers, The State University of New Jersey,
607 Taylor Road, Piscataway, New Jersey 08854-8065*

S. Banerjee, A. Kornienko, and J. G. Brennan
*Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey,
610 Taylor Road, Piscataway, New Jersey 08854-8087*

S. Chen and D. Smith
*Department of Chemistry, Clemson University, Clemson, South Carolina 29634-0973 and Center
for Optical Materials Science and Engineering Technologies, Clemson University,
Clemson, South Carolina 29634-0973*

J. Ballato
*School of Materials Science and Engineering, Center for Optical Materials Science and Engineering
Technologies (COMSET), Clemson University, Clemson, South Carolina 29634-0971*

The infrared fluorescence and optical gain characteristics of optically transparent nanocomposites consisting of $(THF)_{14}Er_{10}S_6Se_{12}I_6$ ("Er10") or $(DME)_2Er(SC_6F_5)_3$ ("Er1") clusters dissolved in a transparent hexafluoroisopropyl (6F) variant of a perfluorocyclobutyl (PFCB)-based fluoropolymer are reported. Under excitation at 980 nm, fluorescence was observed at 1540 nm from both Er10 and Er1 with a 3dB bandwidth of 96 and 60 nm, respectively. The maximum gain computed for Er10 and Er1 was 2.8 and 0.021 dB/cm, respectively. The corresponding threshold pump powers for Er10 and Er1 were calculated to be 1.7 and 0.2 mW, respectively. These computations are consistent with gain characteristics measured by the amplified spontaneous emission technique and suggest that these nanocomposites are promising materials for active optical devices. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2170433]

Lanthanide-based materials are found in a wide range of devices including displays, lasers, optical amplifiers, and taggants because of their attractive luminescent properties. To effect high emission, traditional low phonon (vibrational) energy inorganic materials (e.g., halides or chalcogenides) are processed as single crystals and glasses in fiber, film, and monolithic form. However, these materials are generally difficult to process, possess poor mechanical properties, require expensive processing methods, and exhibit low chemical and thermal stability. Polymer-based materials offer the opportunity to replace traditional inorganic materials since they have attractive mechanical properties, high chemical durability, good thermal stability, and can easily be processed with well-established cost-effective methods to derive the desired forms. The incorporation of molecular lanthanide compounds into polymers include systems such as $Nd(HFA-D)_3$ in poly(methylmethacrylate (PMMA),[1] neodymium octanoate $[Nd(OCA)_3]$ in PMMA,[2,3] Nd tetrakis (benzoyltrifluoroacetonate)in various matrices,[4] $Er(DBM)_3$phen in PMMA,[5,6] Er poly (perfluorobutenyvinylether) in (PF-plastic),[7] Er tetrakis (benzoyltrifluoroacetonate) in various organic hosts,[4] $Eu(TFAA)_3$ in PMMA,[8] $Eu(DBM)_3$ in PMMA,[9] Yb–Er co-doped pentanedione in epoxy novolak resin,[10] Nd-doped polyimide,[11] and Nd chelates in various organic hosts.[12,13] The optical properties of plastic optical fibers containing these lanthanide complexes[14] fail to exhibit promising emission characteristics. Erbium organometallics

typically exhibit lifetimes for the $^4I_{13/2}$ excited state in the μs regime, resulting in low radiative quantum efficiency on the order of 0.01–0.1%.[15–19] These low quantum efficiencies are attributed to the presence of high frequency vibrational bands, such as C–H, O–H, or N–H bonded to Er^{3+}, which reduce emission lifetimes by multiphonon relaxation.

Our approach to obviating these difficulties has been to utilize rare-earth-containing low-vibrational energy materials (e.g., halides and chalcogenides). For example, we have reported on a variety of lanthanide-doped halide, chalcogenide, and chalco-halide nanoparticles and molecular clusters that exhibit excellent fluorescence characteristics.[20–24] LaF_3 and $LaCl_3$ nanoparticles doped with Pr^{3+} or Dy^{3+} that exhibit quantum efficiencies in excess of 70% at 1.3 μm.[22] have been synthesized. More recently, $(THF)_{14}Er_{10}S_6Se_{12}I_6(Er10)$[20] and $(DME)_2Er(SC_6F_5)_3(Er1)$[21] were reported with quantum efficiencies of 78 and 75%, respectively, at 1.5 μm. To our knowledge, these latter materials are the first and only Er-based molecular compounds that have millisecond decay times and radiative quantum efficiencies comparable to inorganic compounds. These exceptional characteristics are attributed to the unique structure of these cluster compounds, where Er-chalcogenide clusters are encapsulated by a shroud of organic ligands. Solubility in organic solvents and polymeric hosts results from the organic ligand encapsulation, which also minimizes light scattering to effect high optical transparency. Such scattering is far more problematic for nanocomposites based on nanoparticles because of the difficulty in dispersing nanoparticles below the length scale of 100 nm while maintaining a high volume

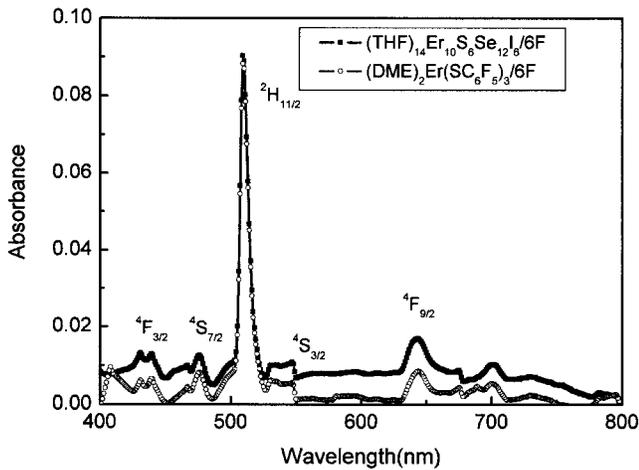[a)]Author to whom correspondence should be addressed; electronic mail: riman@rci.rutgers.edu

FIG. 1. Optical absorption spectrum of $(THF)_{14}Er_{10}S_6Se_{12}I_6/6F$ and $(DME)_2Er(SC_6F_5)_3/6F$ nanocomposite films.

FIG. 2. Comparison of the emission spectra for (●) $(THF)_{14}Er_{10}S_6Se_{12}I_6/6F$, (□) $(DME)_2Er(SC_6F_5)_3/6F$ nanocomposite films.

percentage of solids. Initial reports on the optical performance of such active nanoparticle polymer waveguides have been reported.[23,24] These nanocomposites offer tremendous opportunities because of their unique wavelengths, bright emissions, and controlled line shape.

In this work, we report the infrared emission and optical gain characteristics of Er10 and Er1 dissolved into a transparent hexafluoroisopropyl (6F, $-[C_{19}O_2F_{12}]n-$)) variant of perfluorocyclobutyl (PFCB)-based fluoropolymers. The PFCB polymer was selected as the host because of its low attenuation in the infrared region relative to the well-known PMMA system. The synthesis and optical properties of 6F polymer have been reported previously.[25–27]

$(THF)_{14}Er_{10}S_6Se_{12}I_6$ and $(DME)_2Er(SC_6F_5)_3$ were prepared according to previously reported procedures.[20,21] Precursor solutions for composite materials were prepared by dissolving different concentrations of erbium compounds in the PFCB matrix (available through Tetramer Technologies, L.L.C., Pendleton, SC). The 6F polymer was dissolved in neat toluene to give a solution concentration of 0.1 g/mL and the Er compounds were added to 1 mL of the polymeric solution over a wide range of concentrations (Er1: 0.025 mmol=0.024 g, 0.05 mmol=0.048 g, 0.1 mmol =0.096 g, 0.2 mmol=0.192 g, and 0.4 mmol=0.384 g. Er10: 0.025 mmol=0.12 g, 0.05 mmol=0.24 g, and 0.1 mmol=0.48 g). Composite films were prepared by casting droplets of suspension with a pipette onto glass slides. The droplets spread under the influence of gravity while the toluene solvent evaporated to form a homogeneous transparent composite film.

Optical absorption measurements of the films were measured using a Perkin–Elmer Lambda 9 double beam spectrophotometer (Perkin Elmer, Wellesley, MA). Emission spectra were recorded by exciting the sample with a 980 nm laser diode in the 90°-excitation geometry (S-980,Coherent, Santa Clara, CA). The emission from the sample was focused onto a 1 m Triax 550 monochromator (Jobin Yvon, Edison, NJ) and detected by a thermoelectrically cooled InGaAs detector. The signal was intensified with a SR 850 DSP lock-in amplifier (Stanford Research System, Sunnyvale, CA) and processed with a computer controlled by the Spectramax software (GRAMS 32, Galactic Corp., Salem, NH).

The optical gain coefficient of powdered samples was measured by the amplified spontaneous emission (ASE)
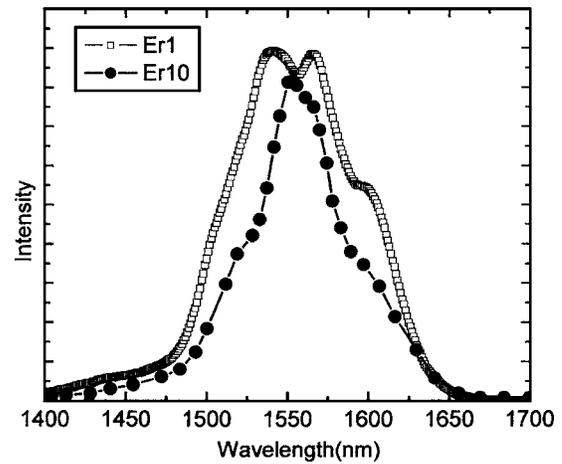
technique in the L-L/2 configuration.[28] For the ASE technique, the emission intensity from different lengths of the pumped region of the sample are compared. Commonly, the comparison is made from two discrete values, which are namely the full length and the half length of the sample (L -L/2 method).[28] It is done by masking the sample surface (or equivalently the pumping beam) with a shutter.

Optical absorption spectra of the Er10/6F and Er1/6F composite films obtained in the visible region with absorption band assignments are shown in Fig. 1. The absorption spectrum shows the typical Er^{3+} absorption transitions, which are comparable in intensity and shape with those of Er10 and Er1 single crystals reported previously.[21] A comparison of the emission spectrum at 1540 nm for two nanocomposite films are shown in Fig. 2. The $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission exhibits a peak due to fluorescence at 1540 nm with a bandwidth (full width at half maximum) of 96 nm and 60 nm for Er10 and Er1, respectively. This broad spectrum may permit a wide gain bandwidth over which optical amplification could occur, which is useful for dense wavelength division multiplexing. With the computed radiative decay time[20] and measured spectral bandwidth, the stimulated emission cross-section of the 1540 nm band was estimated to be 0.86×10^{-20} cm²(Er10/6F) and 1.4×10^{-20} cm²(Er1/6F). The reported values of stimulated emission cross-section of Er^{3+} in other doped polymers were in the range of 3.5×10^{-20} to 5.8×10^{-20} cm².[4–7] Using the measured optical parameters for the Er complexes, an estimate can be made for the optical gain and threshold pump power for a waveguide amplifier. Our numerical simulation utilized a planar waveguide configuration with a core dimension of 2 $\times 1$ μm^2 for either Er10/6F or Er1/6F nanocomposites.

The optical gain was estimated using the following approach. Rate equations were reduced to those of a quasi-two-level system assuming that the population of the $^4I_{11/2}$ state decayed rapidly to the $^4I_{13/2}$ state.[29] The steady-state solutions of the rate equations yielded the populations of the $^4I_{13/2}$ excited state (N_e) and the ground state $^4I_{15/2}$(N_g). N_e and N_g are given as follows: $N_e=R_e/W_e+R_e$ and $N_g =W_e/W_e+R_e$, where $R_e=\sigma_a P\lambda/(hca)$ is the Er^{3+} excitation rate, $W_e=(\tau_e)^{-1}$ the Er^{3+} decay rate, P is the pump power in the waveguide, σ_a is the absorption cross-section at the pumping wavelength (980 nm), λ is the excitation wavelength, and a is the wave-guide cross-section. The optical
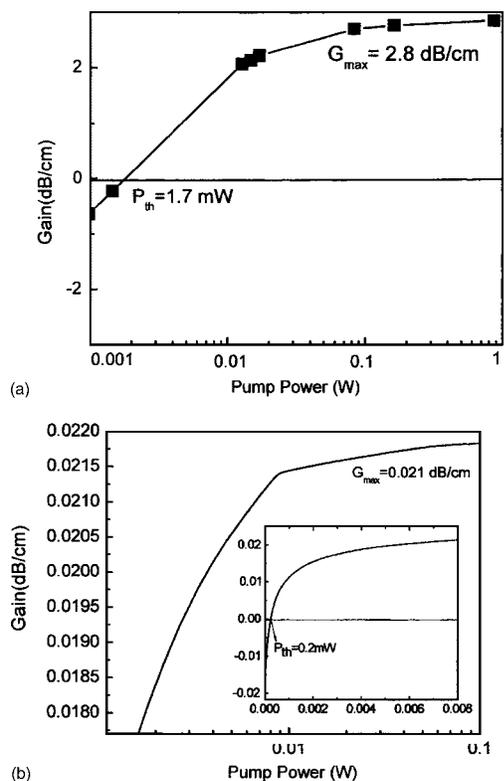
FIG. 3. Optical gain as a function of the pump power in (a) $(THF)_{14}Er_{10}S_6Se_{12}I_6$/6F and (b) $(DME)_2Er(SC_6F_5)_3$/6F nanocomposite films.

gain (dB/cm) was estimated from the expression $10 \log_{10}(I/I_0)$, where I_0 is the incident intensity and the transmitted intensity is given by $I = I_0 \exp(kx)$, where x is the length of the waveguide and k is the gain coefficient. The steady-state solutions were used to compute k as follows: $k = \sigma_e \{N_e - N_g\} N\alpha$, where N is the Er^{3+} concentration, σ_e is the emission cross section, and α is the fraction of the light confined in the film. The numerically estimated gain characteristics for Er10 and Er1 are shown in Fig. 3 and were calculated using $\alpha = 0.4$ and a film cross-section of $2 \times 1 \ \mu m^2$.

The maximum gain obtained for Er10 and Er1 is 2.8 and 0.021 dB/cm, respectively, with a corresponding threshold pump power of 1.7 and 0.2 mW. The predicted optical gain coefficients agree with the measured values of 2.5 dB/cm and 0.02 dB/cm obtained independently from ASE measurements. These threshold values are many times smaller than other reported Er-based organic complexes, which are on the order of 900 mW due to the very low fluorescence decay time of the 1550 nm band. It should be noted that this threshold power is comparable to the 1.4 mW reported for an Er-polydendate cage. However, in this case the pumping is done through the absorption of the band aromatic ligand in the molecule at 287 nm.[8] This mechanism of energy transfer facilies a low pump threshold because of the high absorbance of this band. Low threshold power corresponding to 1.5 mW has also been reported for inorganic systems, such as Er-doped silicates or Al_2O_3 waveguides.[30] The approximate 100-fold reduction in optical gain in Er1/6F relative to Er10/6F is due in part to the 10-fold reduction in Er concentration for Er1. Other factors, such as energy transfer, upconversion, and scattering, could play a role in creating the significant differences in gain observed between these two molecules.

In conclusion, chalcogen-bound Er clusters dissolved in fluoropolymer composite materials emit strongly at 1544 nm. Coordination of organic substituents to the Er gives organosolubility in fluoropolymers to effect excellent transmission. These nanocomposites have emission and optical gain comparable to conventional inorganic systems.

[1] K. Kuriki, T. Kobayashi, N. Imai, T. Tamura, S. Nishihara, A. Tagaya, Y. Koike, and Y. Okamoto. IEEE Photonics Technol. Lett. **12**, 989 (2000).
[2] X. Xu, Opt. Commun. **225**, 55 (2003).
[3] Q. Zhang, H. Ming, and Y. Zhai, J. Appl. Polym. Sci. **62**, 887 (1996).
[4] C. Koeppen, S. Yamada, G. Jiang, A. F. Garito, and L. R. Dalton, J. Opt. Soc. Am. B **14**, 155 (1997).
[5] Z. Zheng, H. Liang, H. Ming, Q. Zhang, and J. Xie. Opt. Commun. **233**, 149 (2004).
[6] H. Liang, Z. Zheng, B. Chen, Q. Zhang, and H. Ming. Mater. Chem. Phys. **86**, 430 (2004).
[7] K. Kuriki, S. Nishihara, Y. Nisizawa, T. Yosinaga, A. Tagaya, Y. Koike, and Y. Okamoto, Opt. Lett. **28**, 570 (2003).
[8] T. Kobayashi, S. Nakatsuka, T. Iwafuji, K. Kuriki, N. Imai, T. Nakamoto, C. D. Claude, K. Sasaki, Y. Koike, and Y. Okamoto. Appl. Phys. Lett. **71**, 2421 (1997).
[9] H. Liang, Q. Zhang, Z. Zheng, H. Ming, Z. Li, J. Xu, B. Chen, and H. Zhao, Opt. Lett. **29**, 477 (2004).
[10] W. H. Wang, E. Y. B. Pun, and K. S. Chan, Appl. Phys. Lett. **84**, 176 (2004).
[11] G. Karve, B. Bihari, and R. T. Chen, Appl. Phys. Lett. **77**, 1253 (2000).
[12] S. Lin, R. J. Feuerstein, and A. R. Mickelson, J. Appl. Phys. **79**, 2868 (1996).
[13] R. T. Chen, M. Lee, S. Natarajan, C. Lin, Z. Z. Ho, and D. Robinson, IEEE Photonics Technol. Lett. **5**, 1328 (1993).
[14] K. Kuriki, Y. Koiki, and Y. Okamoto, Chem. Rev. (Washington, D.C.) **102**, 2347 (2002).
[15] G. A. Hebbink, D. N. Reinboudt, and F. C. J. M. van Veggel, J. Org. Chem. **66**, 4101 (2001).
[16] L. H. Sloof and A. Polman. J. Appl. Phys. **83**, 497 (1998).
[17] M. P. O. Wolbers, F. C. J. M van Veggel, B. H. M. Snellink-Ruel, J. W. Hofstraat, F. A. J. Geurts, and D. N. Reinhoudt, J. Am. Chem. Soc. **119**, 138 (1997).
[18] M. P. O. Wolbers, F. C. J. M. van Veggel, F. G. A. Peters, E. S. E. van Beelen, J. W. Hofstraat, F. A. J. Geurts, and D. N. Reinhoudt, Eur. J. Chem. **4**, 772 (1998).
[19] Y. Hasegawa, T. Okhubo, K. Sogabe, Y. Kawamura, Y. Wada, N. Nakashima, and S. Yanagida. Angew. Chem., Int. Ed. **39**, 357 (2000).
[20] A. Kornienko, T. J Emge, G. A. Kumar, R. E. Riman, and J. G. Brennan, J. Am. Chem. Soc. **127**, 3501 (2005).
[21] G. A Kumar, S. Banerjee, A. Kornienko, J. G. Brennan, and R. E. Riman, Chem. Mater. **17**, 5130 (2005).
[22] J. Ballato, R. E. Riman, and E. Snitzer, Opt. Lett. **22**, 691(1997).
[23] R. Dekker, D. J. W. Klunder, A. Borreman, M. B. J. Diemeer, J. W. Stouwdam, and F. C. J. M van Veggel, Appl. Phys. Lett. **85**, 6104 (2004).
[24] G. A. Kumar, C. W. Chen, S. Chen, D. Smith, J. Ballato, and R. E. Riman, Appl. Phys. Lett. **86**, 1 (2005).
[25] D. Smith, S. Chen, S. Kumar, J. Ballato, C. Topping, and S. Foulger, Adv. Mater. (Weinheim, Ger.) **14**, 1585 (2002).
[26] J. Ballato, D. Smith, and S. Foulger, J. Opt. Soc. Am. B **20**, 1838 (2003).
[27] J. Ballato, D. Smith, and S. Foulger, J. Opt. Soc. Am. B **21**, 958 (2004).
[28] C V. Shank, Rev. Mod. Phys. **47**, 649 (1975).
[29] R. Reisfeld and C. K. Jorgensen, *Lasers and Excited States of Rare Earths* (Springer, New York, 1977).
[30] G. Nykolak, M. Haner, P. C. Becker, J. Schmulovich, and Y. H. Wong, IEEE Photonics Technol. Lett. **5**, 1014 (1993).