

Optical properties of a transparent $\text{CaF}_2:\text{Er}^{3+}$ fluoropolymer nanocomposite

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We report the observation of Er^{3+} fluorescence in an optically transparent $\text{CaF}_2:\text{Er}^{3+}$ perfluorocyclobutyl-based fluoropolymer composite. Under 980 nm excitation, fluorescence was observed at 1560 nm with a bandwidth of 93 nm. A quantitative analysis of the radiative properties yielded a radiative quantum efficiency of 29% corresponding to a measured lifetime of 4 ms and theoretical radiative decay time of 13.8 ms. Further, the estimated stimulated emission cross section was calculated to be $3 \times 10^{-20} \text{ cm}^2$, and the maximum optical gain from the composite was estimated to be 1.78 dB/cm with a pump threshold of 1.1 mW. This estimate demonstrates that it is possible to use polymer nanocomposites for active optical devices. © 2005 American Institute of Physics. [DOI: 10.1063/1.1947891]

Nanomaterials are receiving a great deal of attention due to their potential for enhanced performance. Accordingly, the total global demand for nanoscale materials, tools, and devices was estimated at \$7.6 billion in 2003 and is expected to grow at an average annual growth rate of 30.6% to reach \$28.7 billion in 2008. The dramatic improvements of the various physical and chemical properties in the nanoregime enable the application of nanocomposite materials for the fabrication of many optical, electronic, and biological devices. It is expected that the introduction of multifunctional optical nanocomposites will reduce the size and cost of many consumer and military devices.

Nanocomposites have great potential as well for optical communication systems where active nanocrystals can be dispersed in a low loss waveguide material. For example, Fuchs *et al.*¹ recently reported the fabrication and optical properties of perfluorocyclobutyl (PFCB)-based waveguides containing InAs/ZnSe and CdSe/ZnS core-shell nanocrystals including emission at 1.5 μm . Similarly, the synthesis and luminescence properties of CdS/SiO₂ core-shell quantum dot poly(methylmethacrylate)(PMMA) polymer composite was reported by Farmer *et al.*² By comparison to quantum dots, rare-earth-doped ceramic nanoparticles are more ideal candidates for active nanostructured materials because of their wider range of excitation and emission bands, which extends from ultraviolet to infrared region. Several reports have been published on the fabrication and optical studies of rare-earth organic complex (chelates)-doped polymer composites, which include Nd (HFA-D)₃ in PMMA,³ neodymium octanoate (NdOCA) in PMMA,^{4,5} Nd tetrakis benzoyltrifluoroacetate (BTF) in various organic solvents,⁶ Er (DBM) 3phen in PMMA,^{7,8} Er-poly (perfluorobutenyvinylether) (PF-plastic),⁹ Er-tetrakis BTF in various organic solvents,⁶ Eu(TFAA)₃ in PMMA,¹⁰ Eu(DBM)₃ in PMMA.¹¹ A summary of the optical properties of most of the plastic optical

fibers containing lanthanide complexes can be seen in the review written by Kuriki *et al.*¹² However, in all of these composite materials since the rare-earth ions are attached to an organic ligand, better fluorescence spectral properties could not be expected. On the other hand, the rare-earth-doped inorganic nanoparticle composites show better optical properties due to the increased surface to volume ratio of the nanoparticles as well as due to the reduced phonon energy of inorganic materials compared to organic analogs. In this letter, we report for the first time, the optical properties of $\text{CaF}_2:\text{Er}^{3+}$ nanocrystals doped into a hexafluoroisopropylidene (6F) PFCB-based polymer composite.

Er-doped CaF_2 samples were prepared in ethylene glycol/water mixtures. The Er^{3+} doping concentration in CaF_2 was 2 mol%. At room temperature, a solution of $\text{Er}(\text{OAc})_3$ (1.2 mmol, Aldrich, Milwaukee, WI) and $\text{Ca}(\text{NO}_3)_2$ (8 mmol, Aldrich, Milwaukee, WI) in 16 ml water was added drop wise into NH_4F (22 mmol, Acros Organics, Morris Plains, NJ) ethylene glycol/water solution while stirring. The volume ratio of ethylene glycol/water was 4.7/1. The reaction mixture was stirred at a refluxing temperature of 140 °C for 2 h and cooled to room temperature. The precipitate was separated by centrifuging (Induction Drive Centrifuge, Model J2-21M, Beckman Instruments, Palo Alto, CA) at 18,000 rpm and 15 min and was washed subsequently with ethanol/water (v/v, 1:1) two times and deionized water (resistivity, 18.2 M Ω cm, Millipore RiOs and Elix water purification systems, Millipore Corporation, Burlington, MA) two times. The product was lyophilized for 48 h (Model FO-20-85 BMP Freezer Dryer, FTS Systems, Inc., Stone Ridge, NY).

A PFCB polymer with hexafluoropropyl derivative in the main chain (6F) was prepared as has been previously reported.¹³ The refractive index of the polymer is approximately 1.4 at 1550 nm. Further, the optical properties of this versatile family of fluoropolymers have been reported previously.^{14,15} Toluene was used as the solvent for the preparation of $\text{CaF}_2:\text{Er}^{3+}$ nanocomposite. The $\text{CaF}_2:\text{Er}^{3+}$ loading was 10 wt % in the 6F:PFCB. 0.168 g of 6F polymer was dissolved in 0.5 ml toluene. 0.0187 g of $\text{CaF}_2:\text{Er}$ was

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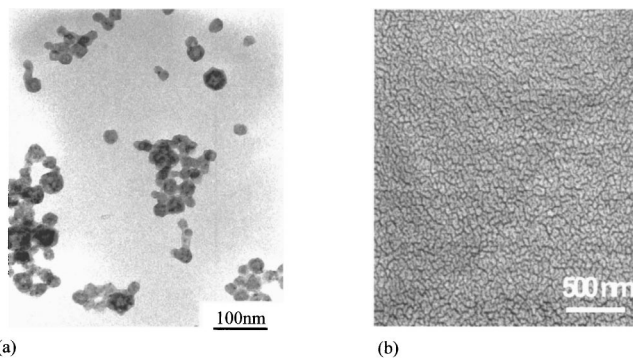


FIG. 1. TEM images of the (a) as prepared (average particle size is 12 nm) and (b) FESEM image of the $\text{CaF}_2:\text{Er}^{3+}/6\text{F}$ composite film.

mixed with 0.5 ml of toluene and ultrasonicated for 15 min. The $\text{CaF}_2:\text{Er}^{3+}/\text{toluene}$ suspension was mixed with 6F polymer solution by ultrasonication for 15 min. The $\text{CaF}_2:\text{Er}^{3+}$ nanocomposite was cast on a glass slide and dried at 70°C in the Isotemp[®] oven (Fischer Scientific, Model 230G, Pittsburgh, PA).

Figure 1(a) shows the transmission electron microscopy (TEM) image of the as-prepared $\text{CaF}_2:\text{Er}^{3+}$ nanocrystals. As observed, the micrograph indicates a spherical morphology with statistical average particle size of ~ 12 nm. In Fig. 2(b) a field emission scanning electron microscope (FESEM) image of the surface of the $\text{CaF}_2:\text{Er}^{3+}/6\text{F}$ composite film is shown which indicates a homogeneous distribution of the nanoparticles inside the polymer nanocomposite.

Figure 2 shows the absorption spectrum of $\text{CaF}_2:\text{Er}^{3+}/6\text{F}$ composite film measured using a double-beam spectrophotometer (Perkin–Elmer Lambda 9, Wellesley, MA). The absorption spectrum shows the typical Er^{3+} absorption transitions, which are comparable in intensity and shape with those of other Er^{3+} -doped hosts.^{16,17}

In order to quantitatively interpret the radiative spectral features of the $\text{CaF}_2:\text{Er}^{3+}/6\text{F}$ nanocomposite, the oscillator strength of the different absorption transitions were measured by a numerical integration technique and fitted with the well known Judd–Ofelt model to obtain the radiative transition probability of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition by the expression¹⁶

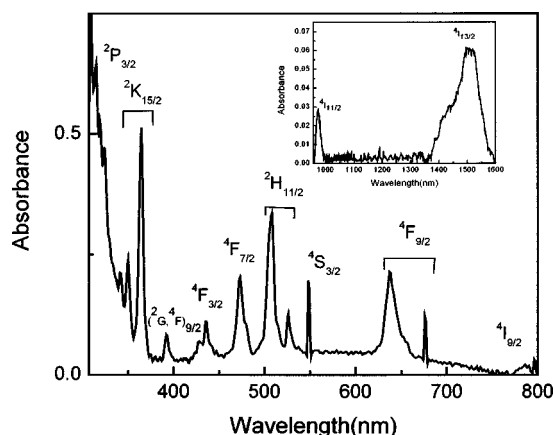


FIG. 2. Absorption spectrum of $\text{CaF}_2:\text{Er}^{3+}/6\text{F}$ composite film of thickness 0.8 mm. The inset shows the near-infrared absorption bands.

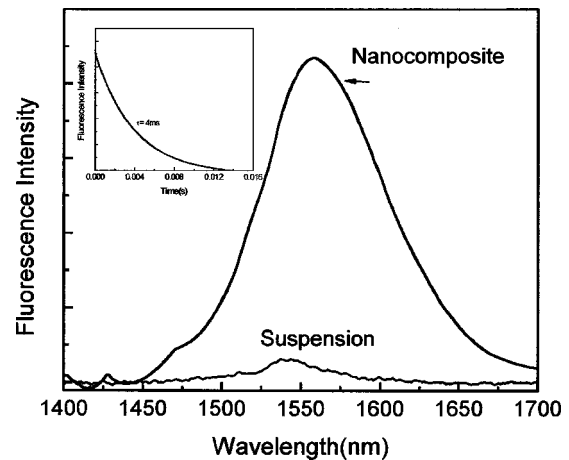


FIG. 3. Emission spectra of Er^{3+} in $\text{CaF}_2/6\text{F}$ composite both in colloidal suspension and nanocomposite form. The inset shows the decay of the emission observed in the nanocomposite sample.

$$A_{\text{rad}}(i \rightarrow j) = \frac{64\pi^4}{3h(2J+1)e^2\lambda^3} \times \left[\frac{n(n^2+2)^2}{9} \right] \sum_{i=2,4,6} \Omega_i \langle ^4I_{13/2} \| U^i \| ^4I_{15/2} \rangle^2, \quad (1)$$

where, λ is the wavelength of the $i \rightarrow j$ transition, n is the refractive index of the nanocomposite, U^i are reduced matrix elements of the $i \rightarrow j$ transition, and Ω_i s are the set of three Judd–Ofelt parameters. The obtained values of Ω_2 , Ω_4 and Ω_6 are, respectively, $7.34 \times 10^{-20} \text{ cm}^2$, $0.8 \times 10^{-20} \text{ cm}^2$, and $1.24 \times 10^{-20} \text{ cm}^2$. With an estimated emission peak wavelength of 1560 nm and the calculated Judd–Ofelt parameters, the radiative transition probability of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition is estimated to be 72 s^{-1} which corresponds to a radiative decay time of 13.8 ms. This lifetime is consistent with the predicted lifetime of Er^{3+} in other hosts.^{16–18}

Figure 3 shows the emission spectrum of $\text{CaF}_2:\text{Er}^{3+}/6\text{F}$ nanocomposite obtained by exciting the sample by a 980 nm diode laser. The fluorescence was collected at 90° excitation geometry and the signal was detected by an InGaAs detector and intensified by a lock-in amplifier. Fluorescence was recorded for both the $\text{CaF}_2:\text{Er}^{3+}/6\text{F}$ solution and the solid film. The $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission has a peak fluorescence of 1560 nm with a band full width at half maximum of 93 nm (11.6 THz). The corresponding values for $\text{CaF}_2:\text{Er}^{3+}$ nanocrystals are, respectively, 1550 nm and 80 nm. This is the highest reported spectral bandwidth in an Er composite: Er (DBM)₃ in PMMA (89 nm)⁷ and Er in PF plastic (28 nm).⁹ Such a broad spectrum enables a wide gain bandwidth product for optical amplification.

With the computed radiative decay time and measured spectral bandwidth, the stimulated emission cross section of the 1560 nm band is estimated to be $3.7 \times 10^{-21} \text{ cm}^2$, which is close to the value of $3.0 \times 10^{-21} \text{ cm}^2$ in $\text{CaF}_2:\text{Er}^{3+}$ nanocrystals.¹⁷ The reported values of stimulated emission cross-section of Er^{3+} in other doped polymers are in the range of 3.5×10^{-20} – $5.8 \times 10^{-20} \text{ cm}^2$.^{7,8}

The fluorescence decay time of the 1560 nm emission was measured by modulating the excitation source at 32 Hz and collecting the averaged signal on a digital oscilloscope. The oscilloscope signal was curve fitted with an exponential function to extract the lifetime (Fig. 2, inset) and the ob-

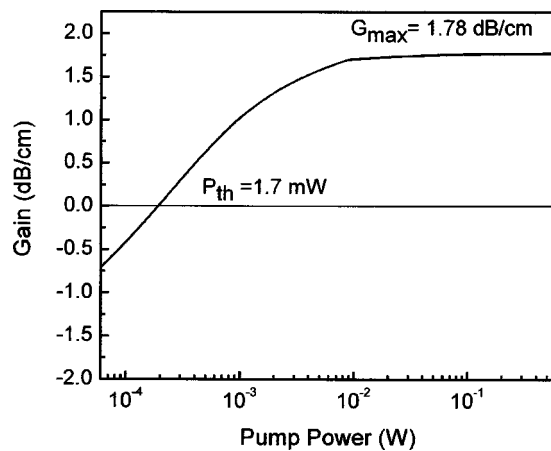


FIG. 4. Predicted optical gain behavior as a function of the pump power.

tained lifetime was 4 ms. Together with the calculated radiative lifetime given above, a luminescence quantum yield of 29% was obtained.

A numerical estimate of the optical gain and threshold pump power is computed following a steady-state solution of the population of the ground state ($N^4I_{15/2}$) and first excited state ($N^4I_{13/2}$) assuming that the population of the pumping state ($^4I_{11/2}$) decays rapidly to the emitting $^4I_{13/2}$ state. The optical gain (dB/cm) is given by $10 \log_{10}(I/I_0)$, where I_0 is the intensity at the beginning of the film and $I=I_0 \exp(kx)$ is the intensity along the length of the film and k is the gain coefficient given by

$$k = \sigma_e(N_{4I_{13/2}} - N_{4I_{15/2}})N\alpha, \quad (2)$$

where N is the Er^{3+} concentration in the composite and α is the estimated fraction of light, which is confined in the film. For a typical value of $\alpha=0.4$ and a film cross section of $2 \times 1 \mu\text{m}^2$, the results obtained are plotted in Fig. 4. The maximum gain obtained is 1.78 dB/cm and the threshold pump power is 1.7 mW. This value is in excellent agreement with the value of 1.8dB/cm obtained for $\text{CaF}_2: \text{Er}^{3+}/6\text{F}$ com-

posite film from amplified spontaneous emission technique.¹⁹ The low pump threshold is interesting for practical applications of planar waveguides.

In conclusion we have reported the first observation of infrared emission of Er^{3+} in an inorganic nanoparticle polymer composite. The luminescence lifetime of Er is 4 ms, and the radiative quantum efficiency is 29%. The low pump threshold enables the possibility of this system as a promising material for use in planar optical amplifier applications.

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